Tetrahedron Letters 53 (2012) 697–701

Contents lists available at SciVerse ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Efficient and chemoselective acetalization and thioacetalization of carbonyls and subsequent deprotection using InF_3 as a reusable catalyst

Sridhar Madabhushi *, Kishore Kumar Reddy Mallu, Narsaiah Chinthala, China Ramanaiah Beeram, Venkata Sairam Vangipuram

Fluoroorganics Division, Indian Institute of Chemical Technology, Hyderabad 500607, India

ARTICLE INFO

Article history:
Received 24 October 2011
Revised 24 November 2011
Accepted 26 November 2011
Available online 3 December 2011

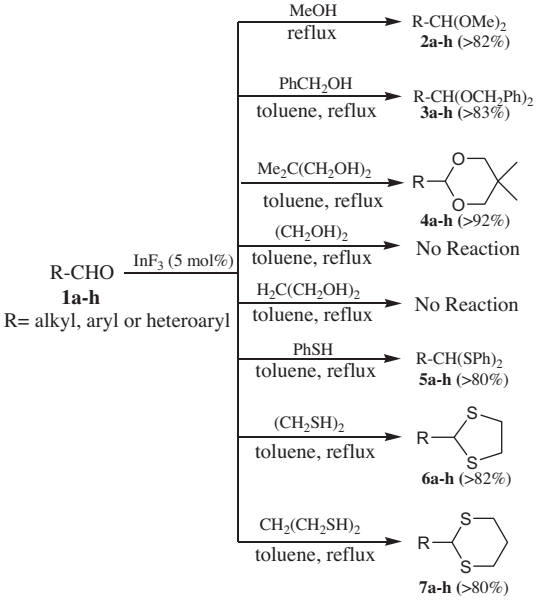
Keywords:
Acetalization
Thioacetalization
InF_3
Catalysis
Deprotection

ABSTRACT

An efficient and chemoselective method for preparation of acetals and dithioacetals of aldehydes and their deprotection under catalysis of InF_3 is described.

Acetalization and thioacetalization are important transformations for the protection of a carbonyl group in multistep organic synthesis. Acetals and dithioacetals tolerate a wide range of nucleophilic, basic and organometallic reagents, reducing agents, and nonacidic oxidants. Dithioacetals or dithianes are also useful for the generation of masked carbonyl anions which are employed in a C–C bond formation reaction known as Corey-Seebach reaction.[1] Hence, studies on acetalization and thioacetalization of carbonyls continue to receive high attention and several methods were developed for acetalization and thioacetalization of carbonyls in the literature.[2] However, there is a dearth of methods for chemoselective acetalization and thioacetalization of carbonyls and the existing methods[3] suffer from one or more of the practical limitations such as long reaction times, high catalyst loading, limited substrate scope, use of toxic reagents and lack of commercial availability of the catalyst. In our recent study, we found an efficient method for selective acetalization and thioacetalization of a variety of aliphatic, aromatic, and heteroaromatic aldehydes using InF_3 as the catalyst as shown in Scheme 1 and under similar conditions, ketones remained unreactive.

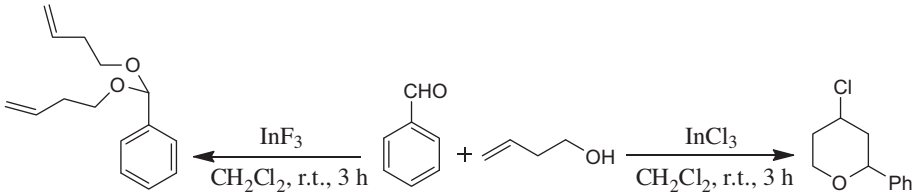
In recent years, Indium (III) reagents, particularly $InCl_3$, $InBr_3$, InI_3, and $In(OTf)_3$, have emerged as promising catalysts for various organic transformations.[4] When compared to these indium reagents, InF_3 has, however, less significance as a catalyst and its applications in organic synthesis have remained scarce in the literature.



Scheme 1. Acetalization and thioacetalization of an aldehyde using InF_3 as a catalyst.

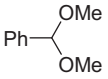
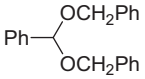
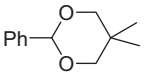
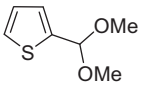
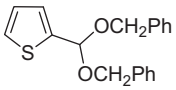
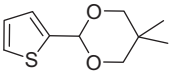
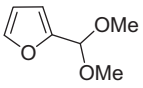
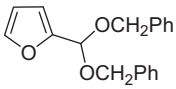
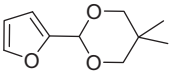
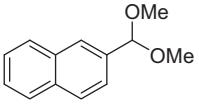
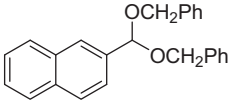
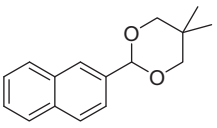
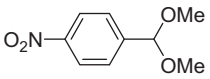
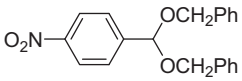
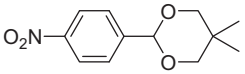
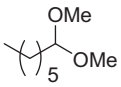
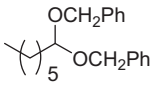
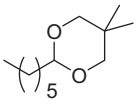
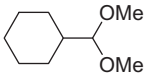
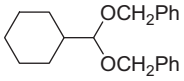
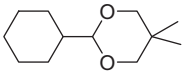
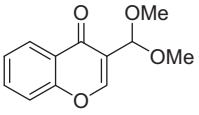
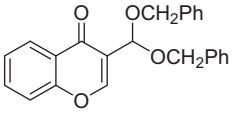
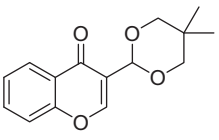
* Corresponding author. Tel.: +91 040 27191772; fax: +91 040 27160387.
E-mail address: smiict@gmail.com (S. Madabhushi).

0040-4039/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2011.11.135



Scheme 2. Reactions of benzaldehyde and homoallyl alcohol in the presence of InF_3 and $InCl_3$.

Table 1
InF_3 catalyzed synthesis of acetals and dioxanes

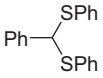
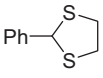
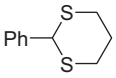
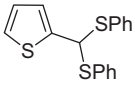
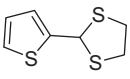
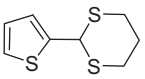
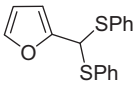
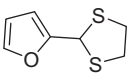
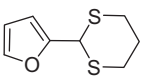
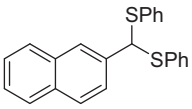
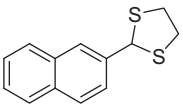
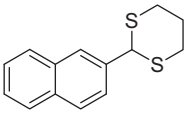
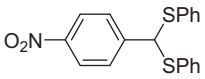
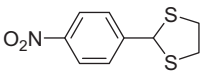
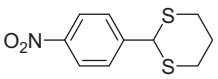
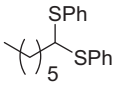
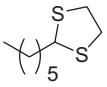
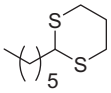
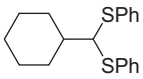
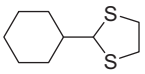
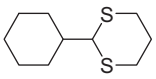
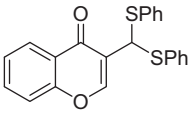
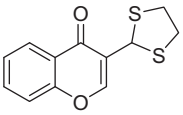
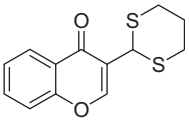
Entry	Acetal **2** % yield[a] (reaction time)	Acetal **3** % yield[a] (reaction time)	Dioxane **4** % yield[a] (reaction time)
a	 87 (5h)	 86 (4h)	 94 (4.5h)
b	 87 (4.5h)	 87 (4h)	 95 (4h)
c	 85 (4.5h)	 85 (4h)	 96 (4h)
d	 85 (5h)	 85 (4.5h)	 98 (4.5h)
e	 82 (4h)	 83 (5h)	 92 (5h)
f	 86 (4h)	 87 (4h)	 95 (3.5h)
g	 86 (4h)	 90 (4h)	 97 (3.5h)
h	 84 (4h)	 86 (5h)	 (95 (5h)

[a] Isolated yields and all products gave satisfactory ^1H, ^{13}C NMR, IR, and Mass spectral data.

Recently, we were interested in the preparation of 4-fluoropyrans by Prins reaction of a homoallylic alcohol and benzaldehyde and we envisioned that InF_3 could possibly promote this reaction as Lee et al.,[5] reported earlier formation of 4-chloropyrons using $InCl_3$. In our study, the expected Prins reaction, however, did not proceed with InF_3 but it was found to catalyze formation of acetal of benzaldehyde with homoallyl alcohol in good yield (86%) as shown in Scheme 2, which is hitherto not known in the literature.

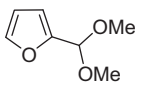
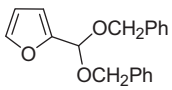
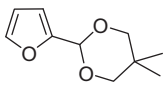
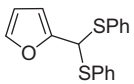
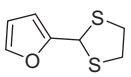
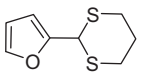
The above observation prompted us to study the scope of acetalization of carbonyl groups with other alcohols under catalysis of InF_3. In our preliminary study, we found a variety of aldehydes such as benzaldehyde **1a**, thiophene-2-carboxaldehyde **1b**, furfural **1c**, 2-napthaldehyde **1d**, 4-nitrobenzaldehyde **1e**, heptanal **1f**, cyclohexanecarboxaldehyde **1g,** and chromone-3-carboxaldehyde **1h** to undergo efficient acetalization with methanol and InF_3 as a catalyst under reflux condition producing corresponding acetals **2a–h** in 82–87% yields. In a similar study, we observed efficient acetalization of aldehydes **1a-h** with benzylalcohol, which gave corresponding dibenzylacetals **3a–h** in 83–90% yields and also with 2,2-dimethyl-1,3-propanediol giving corresponding dioxanes

Table 2
InF_3 catalyzed synthesis of dithioacetals, dithiolanes, and dithianes

Entry	Thioacetal **5** % yield[a] (reaction time)	Dithiolanes **6** % yield[a] (reaction time)	Dithiane **7** % yield[a] (reaction time)
a	 85 (3h)	 85 (5h)	 87 (4h)
b	 87 (2,5h)	 85 (4h)	 85 (4h)
c	 86 (2.5h)	 85 (4h)	 87 (4h)
d	 85 (3h)	 86 (5h)	 85 (3.5h)
e	 80 (4h)	 82 (5h)	 80 (4.5h)
f	 85 (3.5h)	 85 6h)	 85 (3.5h)
g	 90 (3h)	 84 (6h)	 83 (4.5h)
h	 84 (4h)	 86 (5h)	 95(3.5h)

[a] Isolated yields and all products gave satisfactory ^1H, ^{13}C NMR, IR, and Mass spectral data.

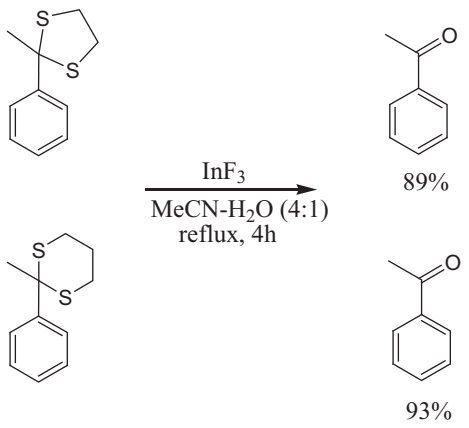
Table 3
Reusability of InF_3 as a catalyst in acetalization and thioacetalization of furfural

Acetal/thioacetal	% Yield[a]				
	1st run	2nd run	3rd run	4th run	5th run
	87	87	85	83	80
	84	84	80	79	79
	96	93	89	89	87
	86	86	82	81	80
	85	85	80	78	78
	85	82	80	79	77

[a] Isolated yields.

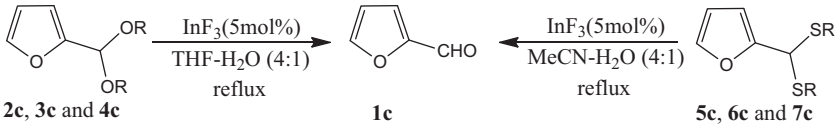
4a–**h** in 92–98% yields as shown in Table 1.[6] In our study, acetalization reactions did not proceed with 1,2-ethanediol and 1,3-propanediol under similar conditions.

Next, we studied the scope of thioacetalization of carbonyls **1a–h** under InF_3 catalysis using benzenethiol, 1,2-ethanedithiol, and

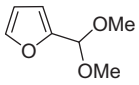
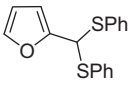
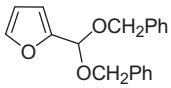
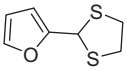
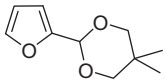
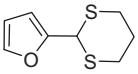


Scheme 3. Deprotection of dithioacetals under InF_3 catalysis.

Table 4
Deprotection of acetals and dithioacetals of furfural using InF_3 as the catalyst



2c, **3c** and **4c** — **1c** — **5c**, **6c** and **7c**

Entry	Acetal	Reaction time (h)	% Yeild[a] of **1c**	Entry	Dithioacetal	Reaction time (h)	% Yeild of **1c**
1		2	87	4		3	90
2		2	85	5		3.5	89
3		2.5	89	6		3.5	93

[a] Isolated yields.

1,3-propanedithiol and obtained corresponding dithioacetals **5a–h** in 80–90% yields, dithiolanes **6a–h** in 82–86% yields and dithianes **7a–h** in 80–87% yields, respectively, under reflux in toluene as shown in Table 2.[7]

In our study, only aldehydes were found to undergo acetalization and thioacetalization under InF_3 catalysis and ketones such as cyclohexanone and acetophenone were found to be unreactive under similar conditions. For example, acetalization and thioacetalization of chromone-3-carboxaldehyde **1h** proceeded selectively on its aldehyde functionality as shown in Table 1 (entries **2h**, **3h,** and **4h**) and Table 2 (entries **5h**, **6h,** and **7h**), respectively. Similarly, when a 1:1 mixture of benzaldehyde and acetophenone was subjected to acetalization with methanol in the presence of InF_3, dimethyl acetal of benzaldehyde was obtained in an 85% yield, while acetophenone was recovered unreacted.

Unlike other indium (III) salts, InF_3 is insoluble in organic solvents and water. In the present study of acetalization and thioacetalization reactions, it was easily separated quantitatively by simple filtration and reused it to observe consistent activity in five consecutive cycles as shown in Table 3.

Unlike acetals,[8] dithioacetals do not easily undergo deprotection by acid catalyzed hydrolysis and oxidative conditions are essentially employed in most of the existing methods for deprotection of dithioacetals.[9] In the literature, only a few methods are available for hydrolytic deprotection of dithioacetals[10] and in the present study, we observed a highly efficient hydrolytic deprotection of dithioacetals of both aldehydes and ketones using InF_3 as a catalyst and aqueous organic solvents as shown in Scheme 3.

In our study, dithioacetals were found to undergo deprotection essentially in aqueous acetonitrile as a solvent,[11] while acetals were found to undergo deprotection also in aqueous mixtures of other organic solvents such as tetrahydrofuran, dichloromethane, and toluene. For example, results observed in deprotection of dithioacetals of furfural (**5c**, **6c,** and **7c)** in 4:1 mixture of acetonitrile-water and deprotection of acetals of furfural **2c**, **3c,** and **4c** in 4:1 mixture of tetrahydrofuran and water is shown in Table 4.

In summary, this work shows a simple and practical method for the chemoselective acetalization and thioacetalization of a variety of aldehydes in high yields using InF_3 as a mild Lewis acid catalyst. In this study, we demonstrated InF_3 as a reusable catalyst for a number of cycles with consistent activity and showed efficient hydrolytic deprotection of acetals and dithioacetals using InF_3 as a catalyst in aqueous organic solvents.

Acknowledgments

K.K.R.M. and C.R.B. are thankful to CSIR, New Delhi and C.N. is thankful to UGC, New Delhi for the award of research fellowships. V.S.V. is thankful to the Director, IICT for the financial support in the form of project fellowship.

References and notes

1. (a) Smith, A. B.; Xian, M. *J. Am. Chem. Soc.* **2006**, *128*, 66–67; (b) Chen, Y. L.; Leguijt, R.; Redlich, H.; Fröhlich, R. *Synthesis* **2006**, 4212–4218; (c) Yus, M.; Najera, C.; Foubelo, F. *Tetrahedron* **2003**, *59*, 6147; (d) Seebach, D.; Corey, E. J. *J. Org. Chem.* **1975**, *40*, 231–237; (e) Corey, E. J.; Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 1075–1077.
2. (a) Cox, D. J.; Smith, M. D.; Fairbanks, A. J. *Org. Lett.* **2010**, *12*, 1452–1455; (b) Wu, Y.-C.; Zhu, J. *J. Org. Chem.* **2008**, *73*, 9522–9524; (c) Procuranti, B.; Connon, S. J. *Org. Lett.* **2008**, *10*, 4935–4938; (d) Gregg, B. T.; Golden, K. C.; Quinn, J. F. *Tetrahedron* **2008**, *64*, 3287–3295; (e) Fujioka, H.; Okitsu, T.; Ohnaka, T.; Li, R.; Kubo, O.; Okamoto, K.; Sawama, Y.; Kita, Y. *J. Org. Chem.* **2007**, *72*, 7898–7902; (f) Polshettiwar, V.; Varma, R. S. *J. Org. Chem.* **2007**, *72*, 7420–7422; (g) Barbasiewicz, M.; Makosza, M. *Org. Lett.* **2006**, *8*, 3745–3748; (h) Kotke, M.; Schreiner, P. R. *Tetrahedron* **2006**, *62*, 434–439; (i) Smith, B. M.; Graham, A. E. *Tetrahedron Lett.* **2006**, *47*, 9317–9319; (j) Ranu, B. C.; Jana, R.; Samanta, S. *Adv. Synth. Cat.* **2004**, *346*, 446–450; (k) Gopinath, R.; Haque, Sk. J.; Patel, B. K. *J. Org. Chem.* **2002**, *67*, 5842–5845; (l) Leonard, N. M.; Oswald, M. C.; Freiberg, D. A.; Nattier, B. A.; Smith, R. C.; Mohan, R. S. *J. Org. Chem.* **2002**, *67*, 5202–5207; (m) Firouzabadi, H.; Iranpoor, N.; Hazarkhani, H. *J. Org. Chem.* **2001**, *66*, 7527–7529; (n) Muthusamy, S.; Babu, S. A.; Gunanathan, C. *Tetrahedron Lett.* **2001**, *42*, 359–362.
3. (a) Yan-Chao, W.; Jieping, Z. *J. Org. Chem.* **2008**, *73*, 9522–9524; (b) Dong, D.; Ouyang, Y.; Yu, H.; Liu, Q.; Liu, J.; Wang, M.; Zhu, J. *J. Org. Chem.* **2005**, *70*, 4535–4537; (c) De, S. K. *Tetrahedron Lett.* **2004**, *45*, 2339–2341; (d) Velusamy, S.; Punniyamurthy, T. *Tetrahedron Lett.* **2004**, *45*, 4917–4920; (e) Karimi, B.; Golshani, B. *Synthesis* **2002**, 784–788.
4. (a) Sridhar, M.; Raveendra, J.; Ramanaiah, C. B.; Narsaiah, C. *Tetrahedron Lett.* **2011**, *52*, 5980–5982; (b) Yadav, J. S.; Antony, A.; George, J.; Basi, V. S. R. *Eur. J. Org. Chem.* **2010**, 591–605; (c) Nakamura, M.; Endo, K.; Nakamura, E. *Org. Lett.* **2005**, *7*, 3279–3281; (d) Araki, S.; Hirashita, T. In *Main Group Metals in Organic Synthesis*; Yamamoto, H., Oshima, K., Eds.; Wiley-VCH: Weinheim, Germany, 2004; pp 323–386. Vol. 1; (e) Ranu, B. C. *Eur. J. Org. Chem.* **2000**, 2347–2356; (f) Li, C. J. *Green Chemistry Frontiers in Benign Chemical Syntheses and Processes*; Oxford University Press: New York, 1998. pp. 234–23.
5. Lee, C.-H. A; Loh, T. –P. *Tetrahedron Lett.* **2006**, *47*, 5980–5982.
6. (a) *Typical procedure for preparation of a dimethoxy acetal* ***2*** *using InF_3 as a catalyst:* Furfural **1c** (0.50 g, 5.2 mmol), methanol (5 ml), and InF_3 (0.04 g, 0.26 mmol), were taken into a 25 ml round-bottomed flask fitted with a condenser and calcium chloride guard tube. The mixture was refluxed for 4.5 h and after completion of the reaction (TLC), the reaction mixture was cooled to room temperature and catalyst was removed by filtration. Catalyst was washed with methanol and the washings were combined with filtrate. The combined organic layer was concentrated under reduced pressure and the resulting crude product was purified by column chromatography using deactivated silica gel (100–200 mesh) with Et_3N and ethyl acetate–hexane (1:20) as eluent to obtain 2-(dimethoxymethyl) furan **2c** (0.63 g, 85%) in the form of a colorless oil and it was characterized by the following spectral data : ^1H NMR (300 MHz, $CDCl_3$):

δ = 7.31–7.30 (d, 1H, J = 2.3 Hz), 6.25–6.24 (dd, 1H, J = 3.0 Hz, 2.3 Hz), 6.18-6.19 (d, 1H, J = 3.0 Hz), 5.71 (s, 1H), 3.24 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.80, 141.72, 110.71, 107.96, 102.31, 51.63; IR (neat): υ 3029, 2928, 1496, 1453, 1366, 1189, 1121, 1069, 977, 832, 748, 699 cm^{-1}; EIMS (m/z, %) : 142 (M^+), 137, 111, 81; Exact mass observed for $C_7H_{10}O_3$: 142.0622 (calculated: 142.0630).

(b) *Typical procedure for preparation of a dibenzyl acetal* ***3*** *using InF_3 as a catalyst:* Furfural **1c** (0.50 g, 5.2 mmol), benzyl alcohol (1.24 g, 11.4 mmol), toluene (5 ml), and InF_3 (0.04 g, 0.26 mmol), were taken into a 25 ml round-bottomed flask fitted with a condenser and calcium chloride guard tube. The mixture was refluxed for 4 h and after completion of the reaction (TLC), the reaction mixture was filtered and the catalyst was washed with toluene. The washings were combined with filtrate and the combined organic layer was concentrated under reduced pressure. The resulting crude product was purified by column chromatography using deactivated silica gel (100–200 mesh) with Et_3N and ethyl acetate–hexane (1:20) as eluent to obtain 2-bis (benzyloxy) methyl) furan **3c** (1.3 g, 85 %) in the form of a colorless oil and it was characterized by the following spectral data : ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.37-7.38 (d, 1H, J = 1.55 Hz), 7.28–7.30 (m, 8H), 7.22–7.25 (m, 2H), 6.48–6.49 (d, 1H, J = 3.0 Hz), 6.32–6.34 (dd, 1H, J = 3.0 Hz, 1.55 Hz), 5.73 (s,1H), 4.57–4.58 (d, 4H, J = 2.26 Hz); ^{13}C NMR(75 MHz, $CDCl_3$): δ = 142.41, 137.65, 128.38, 127.78, 127.62, 126.81, 110.09, 108.75, 95.30, 67.21; IR(neat): υ 3030, 2925, 1494, 1452, 1205, 1079, 1014, 911, 737, 697, 594 cm^{-1} ; EIMS (m/z, %) : 294 (M^+), 187, 107, 91; Exact mass observed for $C_{19}H_{18}O_3$: 294.1261 (calculated: 294.1256).

(c) *Typical procedure for preparation of a dioxane* ***4*** *using InF_3 as a catalyst:* Furfural **1c** (0.50 g, 5.2 mmol), 2,2-dimethylpropane-1,3-diol (0.64 g, 6.2 mmol), toluene (5 ml), and InF_3 (0.04 g, 0.26 mmol), were taken into a 25 ml round-bottomed flask fitted with a condenser and calcium chloride guard tube. The mixture was refluxed for 4 h and after completion of the reaction (TLC), the reaction mixture was filtered and the catalyst was washed with toluene. The washings were combined with the filtrate and the combined organic layer was concentrated under reduced pressure. Purification of the crude product by column chromatography using deactivated silica gel (100–200 mesh) with Et_3N and ethyl acetate–hexane (1:20) as eluent gave 2-(furan-2-yl)-5,5-dimethyl-1,3-dioxane **4c** (0.90 g, 96%) in the form of a white solid and it was characterized by the following spectral data : ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.33–7.35(m,1H), 6.38–6.39(d,1H, J = 3.0 Hz), 6.31–6.33(m, 1H), 5.40(s, 1H), 3.69–3.72(d, 2H, J = 11.33 Hz), 3.54–3.57(d, 2H, J = 11.33 Hz), 1.26 (s, 3H), 0.78 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 150.81, 141.94, 109.85, 106.96, 95.78, 71.30, 30.03, 22.69, 21.54; IR (neat): υ 3056, 2952, 1508, 1466, 1393, 1343, 1232, 1173, 1099, 1015, 830.35, 746 cm^{-1}; EIMS(m/z,%): 182(M^+), 117, 91, 69; Exact mass observed for $C_{10}H_{14}O_3$: 182.0937 (calculated: 182.0943).

(d) Characterization data for new compounds:

Compound **3b:** ^{1}H NMR(300 MHz, $CDCl_3$): δ = 7.29–7.31 (m, 8H), 7.26–7.27 (d, 1H, J = 0.94 Hz), 7.21–7.25 (m, 2H), 7.04–7.05 (d, 1H, J = 3.77 Hz), 6.89–6.92 (dd, 1H, J = 3.77 Hz, 0.94 Hz), 5.93(s, 1H), 4.61(s, 4H); ^{13}C NMR(75 MHz, $CDCl_3$): δ = 147.35, 135.63, 127.39, 126.91, 126.43, 125.96, 125.13, 124.45, 96.86, 67.93; IR (neat): υ 3059, 2965, 1510, 1359, 1235, 1185, 1075, 963, 834, 748 cm^{-1}; EIMS (m/z,%): 310 (M^+), 219, 203, 112, 91; Exact mass observed for $C_{19}H_{18}O_2S$: 310.1034 (calculated: 310.1028).

Compound **3h:** ^{1}H NMR(300 MHz, $CDCl_3$): δ = 7.98–8.02 (d, 1H, J = 9.65 Hz), 7.71–7.76 (m, 5H), 7.63 (s, 1H), 7.28–7.36 (m, 8H), 5.63 (s, 1H), 4.56 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 180.10, 157.12, 149.56, 137.45, 130.64, 128.79, 127.69, 127.36, 123.94, 122.68, 121.22, 120.61, 115.67, 97.32, 68.89; IR (neat): υ 3054, 2940, 1743, 1485, 1366, 1204, 1065, 954, 790 cm^{-1}; EIMS(m/z,%): 372 (M^+), 265, 158, 91; Exact mass observed for $C_{24}H_{20}O_4$: 372.1355 (calculated: 372.1362).

Compound **4b:** ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.24–7.26 (dd, 1H, J = 5.28 Hz, 3.77 Hz), 7.06–7.07(d, 1H, J = 3.77 Hz), 6.93–6.96(dd, 1H, J = 5.28 Hz, 3.77 Hz), 5.57 (s,1H), 3.70–3.74 (d, 2H, J = 11.33 Hz), 3.57–3.60 (d, 2H, J = 11.33 Hz), 1.27 (s, 3H), 0.79 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.20, 126.22, 125.41, 124.84, 98.05, 77.20, 22.79, 21.69; IR (neat): υ 3106, 2960, 1540, 1449, 1377, 1309, 1218, 1186, 1021, 844, 778 cm^{-1}; EIMS(m/z,%): 198(M^+), 127, 113, 85, 56; Exact mass observed for $C_{10}H_{14}O_2S$: 198.0708 (calculated: 198.0715).

Compound **4d:** ^{1}H NMR(300 MHz, $CDCl_3$): δ = 7.90(s, 1H), 7.76–7.82(m, 3H), 7.55–7.58 (d, 1H, J = 8.49 Hz), 7.39–7.44 (m, 2H), 5.48 (s, 1H), 3.75–3.80 (d, 2H, J = 10.95 Hz), 3.62–3.67 (d, 2H, J = 10.95 Hz), 1.31 (s, 3H), 0.81 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 135.80, 132.95, 128.26, 128.06, 127.56, 126.11, 125.91, 125.38, 123.72, 101.70, 77.62, 23.01, 21.79; IR(neat): υ 3048, 2922, 1577, 1471, 1362, 1270, 1178, 1063, 860, 752 cm^{-1}; EIMS (m/z, %): 242 (M^+), 155, 127, 91, 55; Exact mass observed for $C_{16}H_{18}O_2$: 242.1298 (calculated: 242.1307).

Compound **4g:** ^{1}H NMR(300 MHz, $CDCl_3$): δ = 4.08–4.10 (d, 1H, J = 4.72 Hz), 3.53–3.57 (d, 2H, J = 10.76 Hz), 3.31–3.35 (d, 2H, J = 10.76 Hz), 1.46–1.79 (m, 6H), 1.04–1.25 (m, 8H), 0.70(s, 3H); ^{13}C NMR(75 MHz, $CDCl_3$): δ = 104.89, 76.99, 42.21, 30.15, 27.19, 26.53, 25.88, 22.94, 21.87; IR (neat): υ 2950, 1453, 1350, 1231, 1194, 841 cm^{-1}; EIMS(m/z,%): 198(M^+), 168, 102, 83; Exact mass observed for $C_{12}H_{22}O_2$: 198.1632 (calculated: 198.1620).

7. (a) *Typical procedure for preparation of a dithioacetal 5 using InF_3 as a catalyst:* Furfural **1c** (0.50 g, 5.2 mmol), thiophenol (1.26 g, 11.4 mmol), toluene (5 ml), and InF_3 (0.04 g, 0.26 mmol), were taken into a 25 ml round-bottomed flask fitted with a condenser and calcium chloride guard tube and the mixture was refluxed for 2.5 h. After completion of the reaction (TLC), the reaction mixture was filtered, catalyst was washed with toluene and the washings were combined with filtrate. The combined organic layer was concentrated and purified by normal column chromatography (silica gel 100–200 mesh, ethyl acetate–hexane = 1:20) to obtain 2-(bis (phenylthio) methyl) furan **5c** (1.34, 86 %) in the form of a colorless oil and it was characterized by the following spectral data : ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35–7.32 (m, 5H), 7.24–7.22 (m, 6H), 6.21–6.20 (d, 1H, J = 3.0 Hz), 6.12–6.10 (d, 1H, J = 3.0 Hz), 5.4 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 151.66, 143.74, 134.30, 132.73, 128.73, 127.89, 126.33, 125.58, 55.63; IR (neat): υ 3058, 2923, 1477, 1438, 1303, 1228, 1069, 1012, 936, 885, 739, 690 cm^{-1} ; EIMS (m/z, %) : 298 (M^+), 189, 122, 100; Exact mass observed for $C_{17}H_{14}OS_2$: 298.0479 (calculated: 298.0486).

(b) *Typical procedure for preparation of a dithiolane 6 using InF_3 as a catalyst:* Furfural **1c** (0.50 g, 5.2 mmol), 1,2-ethanedithiol (0.58 g, 6.2 mmol), toluene (5 ml), and InF_3 (0.04 g, 0.26 mmol), were taken into a 25 ml round-bottomed flask fitted with a condenser and calcium chloride guard tube and the mixture was refluxed for 4 h. After completion of the reaction (TLC), the reaction mixture was filtered, catalyst was washed with toluene and the washings were combined with filtrate. The combined organic layer was concentrated and purified by normal column chromatography (silica gel 100–200 mesh, ethyl acetate–hexane = 1:20) to obtain 2-(1,3-dithiolan-2-yl)furan **6c** (0.76 g, 85 %) in the form of a colorless oil and it was characterized by the following spectral data : ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.31–7.32 (m, 1H), 6.22–6.25 (m, 2H), 5.55 (s, 1H), 3.34–3.42 (m, 2H), 3.24–3.32 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.10, 142.17, 110.08, 106.76, 47.22, 38.84; IR (neat): υ 3117, 2925, 1585, 1499, 1421, 1276, 1171, 1147, 1010, 936, 851, 739 cm^{-1} ; EIMS (m/z, %) : 172(M^+), 143, 111, 105; Exact mass observed for $C_7H_8OS_2$: 172.0009 (calculated: 172.0017).

(c) *Typical procedure for preparation of dithiane 7 using InF_3 as a catalyst:* Furfural **1c** (0.50 g, 5.2 mmol), 1,3-propanedithiol (0.58 g, 6.2 mmol), toluene (5 ml), and InF_3 (0.04 g, 0.26 mmol), were taken into a 25 ml round-bottomed flask fitted with a condenser and calcium chloride guard tube and the mixture was refluxed for 4 h. After completion of the reaction (TLC), the reaction mixture was filtered, catalyst was washed with toluene and the washings were combined with filtrate. The combined organic layer was concentrated and purified by normal column chromatography (silica gel 100–200 mesh, ethyl acetate–hexane = 1 : 20) to obtain 2-(1,3-dithian-2-yl)furan **7c** (0.84 g, 87%) in the form of a colorless oil and it was characterized by the following spectral data : ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.33–7.34 (d, 1H, J = 2.27 Hz), 6.35–6.36 (d, 1H, J = 3.0 Hz), 6.30–6.31 (dd, 1H, J = 3.0 Hz, 2.27 Hz), 5.13 (s,1H), 2.86–2.98 (m, 4H), 1.95–2.17 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): 152.00, 141.88, 110.58, 107.75, 41.95, 30.22, 25.25; IR (neat): υ 2925, 1496, 1420, 1274, 1161, 1069, 1010, 939, 878, 740, 642 cm^{-1}; EIMS (m/z, %) : 186 (M^+), 141, 127, 111; Exact mass observed for $C_8H_{10}OS_2$: 186.0178 (calculated: 186.0173).

(d) Characterization data for new compounds:

Compound **5b:** ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.33–7.37 (m, 4H), 7.20–7.25 (m, 6H), 7.15–7.18 (d, 1H, J = 5.09 Hz), 6.86–6.88 (d, 1H, J = 3.58 Hz), 6.78–6.81 (dd, 1H, J = 5.09 Hz, 3.58 Hz), 5.6 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.73, 134.20, 132.73, 128.73, 127.89, 126.33, 125.57, 96.13, 55.62; IR (neat): υ 3062, 2924, 1464, 1340, 1231, 1120, 1015, 934, 740 cm^{-1}; EIMS (m/z, %): 314 (M^+), 205, 84, 77, 56; Exact mass observed for $C_{17}H_{14}S_3$: 314.0245 (calculated: 314.0258).

Compound **5h:** ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.24–8.27 (dd, 1H, J = 9.82 Hz, 8.31 Hz), 8.02 (s, 1H), 7.61–7.67 (m, 1H), 7.38–7.43 (m, 6H), 7.18–7.27 (m, 6H), 5.94 (s,1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 179.51, 157.23, 135.83, 131.28, 130.74, 129.88, 127.87, 127.07, 126.13, 125.78, 122.93, 116.45, 115.21, 46.67; IR (neat): υ 3062, 2928, 1728, 1496, 1366, 1187, 1069, 976, 832, 748 cm^{-1}; EIMS (m/z, %): 376 (M^+), 267, 189, 102, 88, 60; Exact mass observed for $C_{22}H_{16}O_2S_2$: 376.0583 (calculated: 376.0592).

Compound **7h:** ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.23–8.26 (d, 1H, J = 7.93 Hz), 8.15 (s, 1H), 7.61–7.67 (m, 1H), 7.36–7.43 (m, 2H), 5.55 (s, 1H), 3.07–3.16 (m, 2H), 2.84–2.91 (m, 2H), 2.14–2.23 (m, 1H), 1.20–1.89 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 178.06, 157.23, 151.64, 135.34, 130.61, 123.92, 117.71, 115.32, 39.04, 32.46, 25.25; IR (neat): υ 3101, 2954, 1732, 1484, 1289, 1184, 1074, 954, 793 cm^{-1}; EIMS (m/z, %) : 264 (M^+), 232, 145, 117, 106; Exact mass observed for $C_{13}H_{12}O_2S_2$: 264.0291 (calculated: 264.0279).

8. (a) Gregg, B. T.; Golden, K. C.; Quinn, J. F. *J. Org. Chem.* **2007**, *72*, 5890–5893; (b) Chang, C. –C.; Liao, B.-S.; Liu, S.-T. *Synlett* **2007**, 283–287; (c) Kumar, R.; Kumar, D.; Chakraborti, A. K. *Synthesis* **2007**, 299–303; (d) Dalpozzo, R.; De Nino, A.; Maiuolo, L.; Procopio, A.; Tagarelli, A.; Sindona, G.; Bartoli, G. *J. Org. Chem.* **2002**, *67*, 9093–9095; (e) Carrigan, M. D.; Sarapa, D.; Smith, R. C.; Wieland, L. C.; Mohan, R. S. *J. Org. Chem.* **2002**, *67*, 1027.
9. (a) Burghardt, T. E. *J. Sulfur Chem.* **2005**, *26*, 411–427; (b) Dalpozzo, R.; De Nino, A.; Maiuolo, L.; Nardi, M.; Procopio, A.; Tagarelli, A. *Synthesis* **2004**, 496–498; (c) Kamal, A.; Reddy, P. S. M. M.; Reddy, D. R. *Tetrahedron Lett.* **2003**, *44*, 2857–2860; (d) Langille, N. F.; Dakin, L. A.; Panek, J. S. *Org. Lett.* **2003**, *5*, 575–578; (e) Nicolaou, K. C.; Mathison, C. J. N.; Montagnon, T. *Angew. Chem., Int. Ed.* **2003**, *42*, 4077–4082; (f) Carrigan, M. D.; Sarapa, D.; Smith, R. C.; Wieland, L. C.; Mohan, R. S. *J. Org. Chem.* **2002**, *67*, 1027–1030.
10. (a) Ganguly, N. C.; Barik, S. K. *Synthesis* **2009**, 1393–1399; (b) McHale, W. A.; Kutateladze, A. G. *J. Org. Chem.* **1998**, *63*, 9924–9931.

11. *Typical procedure for deprotection of a dithioacetal:* 2-(1,3-dithiolan-2-yl)furan **6c** (0.5 g, 2.9 mmol), InF_3 (24 mg, 0.14 mmol), acetonitrile (8 ml), water (2 ml) were taken into a 50 ml round bottomed flask fitted with a condenser and the mixture was refluxed for 3.5 h. After completion of the reaction (TLC), acetonitrile was removed under reduced pressure and extracted with diethylether (2 × 5 ml). The combined organic layer was washed with brine (1 × 5 ml), concentrated and the crude product was purified by normal column chromatography to obtain furfural **1c** (0.25 g, 89 %), which gave spectral data (^{1}H NMR, IR, and Mass) identical to that of the authentic sample.