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Enantioselective Carbonyl Allylation, Crotylation and *tert*-Prenylation of Furan Methanols and Furfurals *via* Iridium Catalyzed Transfer Hydrogenation

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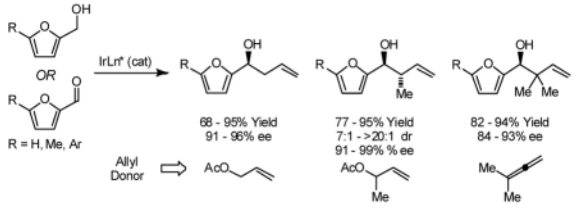
Abstract



5-Substituted-2-furan methanols **1a–1c** are subject to enantioselective carbonyl allylation, crotylation and *tert*-prenylation upon exposure to allyl acetate, α-methyl allyl acetate or 1,1,-dimethylallene in the presence of an *ortho*-cyclometallated iridium catalyst modified by (*R*)-Cl,MeO-BIPHEP, (*R*)-C3 -TUNEPHOS and (*R*)-C3-SEGPHOS, respectively. In the presence of isopropanol, but under otherwise identical conditions, the corresponding substituted furfurals **2a–2c** are converted to identical products of allylation, crotylation and *tert*-prenylation. Optically enriched products carbonyl allylation, crotylation and reverse prenylation **3b**, **4b** and **5b** were subjected to Achmatowicz rearrangement to furnish the corresponding γ-hydroxy-β-pyrones **6a–6c**, respectively, with negligible erosion of enantiomeric excess.

In the course of studies on C-C bond forming hydrogenations and transfer hydrogenations,[1] we found that cyclometallated iridium *C,O*-benzoates modified by chiral phosphine ligands are effective catalysts for the enantioselective reductive coupling of allyl acetate, α-methyl allyl acetate and 1,1-dimethylallene to carbonyl electrophiles to furnish products of carbonyl allylation,[2a,b,e–h] crotylation[2c,f] and *tert*-prenylation,[2d,f] respectively. For such "*C-C bond forming transfer hydrogenations*", isopropanol serves as the terminal reductant for additions to preformed aldehyde electrophiles. Remarkably, primary alcohols serve dually as hydrogen donors and aldehyde precursors, enabling asymmetric carbonyl allylation, crotylation and *tert*-prenylation directly from the alcohol oxidation level. Here, hydrogen exchange between an alcohol-unsaturate redox pair enables generation of an electrophile-nucleophile pair. In this way, non-stabilized carbanion equivalents are generated in the absence of stoichiometric metallic reagents. This strategy for carbonyl allylation differs significantly from conventional

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Supporting Information Available: Spectral data for all new compounds, including scanned images of ^{1}H and ^{13}C NMR spectra. Scanned images of chiral stationary phase HPLC data. Single crystal X-ray diffraction data for the Ir(BIPHEP)(η-C_3H_5)(*C,O*-$O_2C_6H_3NO_2$). This material is available free of charge *via* the internet at http://pubs.acs.org.

carbonyl protocols, which exploit stoichiometric quantities of allylmetal reagents or metallic reductants.[3],[4],[5].

In connection with studies toward the syntheses of the mitochondrial electron transport inhibitors ajudazols A and B,[6] one of the present authors required a highly enantioselective method for the crotylation of a substituted furfural. Although the enantioselective allylation of furfurals has been achieved using stoichiometric allylmetal reagents,[7] Denmark reports the only catalytic method for enantioselective crotylation and reverse prenylation of furfural.[7f,n] Given the broad utility of furans as building blocks in organic synthesis,[8] we sought to further evaluate the scope of our emergent allylation methodology in a systematic study of allylation, crotylation and reverse prenylation substituted furfurals from both the alcohol and aldehyde oxidation levels. Here, we disclose that 5-substituted-2-furan methanols **1a–1c** are subject to highly enantioselective carbonyl allylation, crotylation and reverse prenylation upon exposure to allyl acetate, α-methyl allyl acetate or 1,1,-dimethylallene, respectively, in the presence of an *ortho*-cyclometallated iridium catalyst modified by (*R*)-Cl,MeO-BIPHEP, (*S*)-C3-TUNEPHOS and (*R*)-C3-SEGPHOS, respectively. Under nearly identical conditions, but in the presence of isopropanol, the corresponding substituted furfurals are converted to identical products of allylation, crotylation and reverse prenylation. Achmatowicz rearrangement of the 5-methyl-2-furan methanol adducts **3b**, **4b**, **5b** is described.[9]

In an initial set of experiments, 5-substituted-2-furan methanols **1a–1c** were subjected to conditions for enantioselective iridium catalyzed carbonyl allylation employing an *ortho*-cyclometallated catalyst generated *in situ* from $[Ir(cod)Cl]_2$, (*R*)-Cl,MeO-BIPEHP and 4-chloro-3-nitrobenzoic acid.[2a,b,e–h] Use of the preformed complex provided comparable yields and selectivities. The products of carbonyl allylation **3a–3c** are formed in good isolated yield with uniformly high levels of optical purity using only two equivalents of allyl acetate as the allyl donor (Table 1). Under the same conditions, but in the presence of 2-propanol, the corresponding 5-substituted-2-furfurals **2a–2c** are converted to an identical set of carbonyl allylation products **3a–3c** in good to excellent isolated yields with uniformly high levels of enantioselectivity. Notably, the parent furans **1a** and **2a** provide slightly lower yields of the homoallylic alcohol **3a**, presumably due to volatility or sensitivity of the furan nucleus with respect to acid promoted degradation during isolation by silica gel chromatography (Table 2).

Enantioselective crotylation of 5-substituted-2-furan methanols **1a–1c** was explored next.[2c,f] Here, the preformed *ortho*-cyclometallated complex generated from $[Ir(cod)Cl]_2$, (*S*)-C3-TUNEPHOS and 4-cyano-3-nitrobenzoic acid provided enhanced yields and selectivities. A further increase in isolated yield resulted from the use of tribasic potassium phosphate as base in the presence of water. Under these conditions, the 5-substituted-2-furan methanols **1a–1c** were converted to the products of crotylation **4a–4c** in good to excellent isolated yield with high levels of *anti*-diastereoselectivity and uniformly high levels of enantioselectivity, as determined by HPLC analysis (Table 3). Under the same conditions, but in the presence of 2-propanol, the corresponding 5-substituted-2-furfurals **2a–2c** are converted to an identical set of carbonyl crotylation products **4a–4c** with notably enhanced levels of *anti*-diastereo- and enantioselectivity (Table 4).

Finally, the enantioselective *tert*-prenylation of 5-substituted-2-furan methanols **1a–1c** was explored using the isolated the *ortho*-cyclometallated catalyst generated from $[Ir(cod)Cl]_2$, (*R*)-SEGPHOS and 4-cyano-3-nitrobenzoic acid.[2d,f] Under remarkably mild conditions, good to excellent isolated yields of **5a–5c** were attended by good levels of asymmetric induction (Table 5). Slightly improved isolated yields and enantioselectivities were observed when the *tert*-prenylated adducts **5a–5c** were generated from the corresponding aldehydes **2a–2c** (Table 6). Thus, allylation, *anti*-crotylation and *tert*-prenylation are achieved from either the alcohol or aldehyde oxidation level with roughly equal facility using 5-substituted-2-furan methanols **1a–1c** or 5-substituted-2-furfurals **2a–2c**, respectively.

The Achmatowicz rearrangement of substituted furan methanols is frequently employing in the total synthesis of natural products.[9b] Accordingly, the optically enriched products of allylation, crotylation and *tert*-prenylation **3b**, **4b** and **5b**, respectively, were subjected to conditions for Achmatowicz rearrangement employing *N*-bromosuccinimide as the oxidant. The corresponding γ-hydroxy-β-pyrones **6a–6c** were formed as diastereomeric mixtures at the lactol center. However, negligible erosion of enantiomeric excess was observed at preexisting stereocenters, as determined by chiral stationary phase HPLC analysis (Scheme 1).

In summary, we report that 5-substituted-2-furan methanols **1a–1c** are subject to enantioselective carbonyl allylation, crotylation and *tert*-prenylation upon exposure to allyl acetate, α-methyl allyl acetate or 1,1,-dimethylallene in the presence of an *ortho*-cyclometallated iridium catalyst modified by (*R*)-Cl,MeO-BIPHEP, (*S*)-C3-TUNEPHOS and (*R*)-C3-SEGPHOS, respectively. In the presence of isopropanol, but under otherwise identical conditions, the corresponding substituted furfurals **2a–2c** are converted to identical products of allylation, crotylation and *tert*-prenylation. Optically enriched products carbonyl allylation, crotylation and reverse prenylation **3b**, **4b** and **5b** engage in Achmatowicz rearrangement to furnish the corresponding γ-hydroxy-β-pyrones in good yield and with negligible erosion of enantiomeric excess at the preexisting stereocenter.

Experimental Section

General Procedure for the Preparation of Adducts 3a–3c from Furan Methanols 1a–1c

To a flame dried re-sealable reaction tube purged with argon and containing a magnetic stirrer, was added $[Ir(cod)Cl]_2$ (6.7 mg, 0.010 mmol, 2.5 mol%), (*R*)-Cl,MeO-BIPHEP (13.0 mg, 0.020 mmol, 5 mol%), 3-nitro-4-chlorobenzoic acid (8.1 mg, 0.040 mmol 10 mol%), Cs_2CO_3 (26.1 mg, 0.080 mmol, 20 mol%) and the furan methanol (0.40 mmol, 100 mol%). THF (2.0 mL, 0.2 M concentration with respect to the furan methanol) and allyl acetate (86 μL, 0.80 mmol, 200 mol%) were added and the reaction mixture was allowed to stir at 100 °C for 24 hours. The reaction mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2) to furnish the corresponding products of allylation **3a–3c**.

General Procedure for the Preparation of Adducts 3a–3c from Furfurals 2a–2c

To a flame dried re-sealable reaction tube purged with argon and containing a magnetic stirrer, was added $[Ir(cod)Cl]_2$ (6.7 mg, 0.010 mmol, 2.5 mol%), (*R*)-Cl,MeO-BIPHEP (13.0 mg, 0.020 mmol, 5 mol%), 3-nitro-4-chlorobenzoic acid (8.1 mg, 0.040 mmol 10 mol%), Cs_2CO_3 (26.1 mg, 0.080 mmol, 20 mol%) and the furfural (0.40 mmol, 100 mol%). THF (2.0 mL, 0.2 M concentration with respect to the furfural), *i*-PrOH (61 μL, 0.80 mmol, 200 mol%) and allyl acetate (86 μL, 0.80 mmol, 200 mol%) were added and the reaction mixture was allowed to stir at 100 °C for 24 hours. The reaction mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2) to furnish the corresponding products of allylation **3a–3c**.

General Procedure for the Preparation of Adducts 4a–4c from Furan Methanols 1a–1c

To a flame dried re-sealable reaction tube purged with argon and containing a magnetic stirrer, was added (*R*)-Ir-complex **I** (20.4 mg, 0.020 mmol, 5 mol%), K_3PO_4 (84.9 mg, 0.40 mmol, 100 mol%), and the corresponding furan methanol (0.40 mmol, 100 mol%). THF (0.2 mL, 2 M concentration with respect to the alcohol), H_2O (36 μL, 2.0 mmol, 500 mol%) and α-methyl allyl acetate (86 μL, 0.80 mmol, 200 mol%) were added and the reaction mixture was allowed to stir at 70 °C for 48 hours. The reaction mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2) to furnish the corresponding products of crotylation **4a–4c**.

General Procedure for the Preparation of Adducts 4a–4c from Furfurals 2a–2c

To a flame dried re-sealable reaction tube purged with argon and containing a magnetic stirrer, was added (*R*)-Ir-complex **I** (20.4 mg, 0.020 mmol, 5 mol%), K_3PO_4 (84.9 mg, 0.400 mmol, 100 mol%), and the corresponding furfural (0.40 mmol, 100 mol%). THF (0.2 mL, 2 M concentration with respect to the aldehyde), H_2O (36 μL, 2.0 mmol, 500 mol%), *i*-PrOH (61 μL, 0.80 mmol, 200 mol%) and α-methyl allyl acetate (86 μL, 0.80 mmol, 200 mol%) were added and the reaction mixture was allowed to stir at 70 °C for 48 hours. The reaction mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2), under the conditions noted, to furnish the corresponding products of crotylation **4a–4c**.

General Procedure for the Preparation of Adducts 5a–5c from Furan Methanols 1a–1c

To a flame dried re-sealable reaction tube purged with nitrogen and containing a magnetic stirrer, was added (*R*)-Ir-complex **II** (5 mol%) and the corresponding furan methanol (100 mol %). Toluene (1 M concentration with respect to the alcohol), 1,1-dimethylallene (200 mol%), and propionaldehyde (5 mol%) were added and the reaction mixture was allowed to stir at 40 °C for 72 hours. The reaction mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2) to furnish the corresponding products of *tert*-prenylation **5a–5c**.

General Procedure for the Preparation of Adducts 5a–5c from Furfurals 2a–2c

To a flame dried re-sealable reaction tube purged with nitrogen and containing a magnetic stirrer, was added (*R*)-Ir-complex **II** (5 mol%) and the corresponding furfural (100 mol%). Toluene (1 M concentration with respect to the aldehyde), 1,1-dimethylallene (200 mol%), and *i*-PrOH (200 mol%) were added and the reaction mixture was allowed to stir at 40 °C for 72 hours. The reaction mixture was concentrated *in vacuo* and purified by flash column chromatography (SiO_2) to furnish the corresponding products of *tert*-prenylation **5a–5c**.

General Procedure for the Achmatowicz Rearrangement of Adducts 3b, 4b, and 5b

Alcohols **3b**, **4b** or **5b** (100 mol%) were dissolved in aqueous THF (THF: H_2O, 4:1, 0.1 M) and the solution was cooled to 0 °C. N-bromosuccinimide (100 mol%) was added portion-wise while maintaining a temperature of 0 °C. After the reaction had gone to completion as determined by TLC analysis, the reaction mixture was diluted with dichloromethane and washed with KI (10% aqueous solution), $Na_2S_2O_4$ (15% aqueous solution), and $NaHCO_3$ (10% aqueous solution), and brine. The organic layer was dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude residue was purified by flash column chromatography (SiO_2) to furnish the corresponding pyrones **6a**, **6b** or **6c**, respectively.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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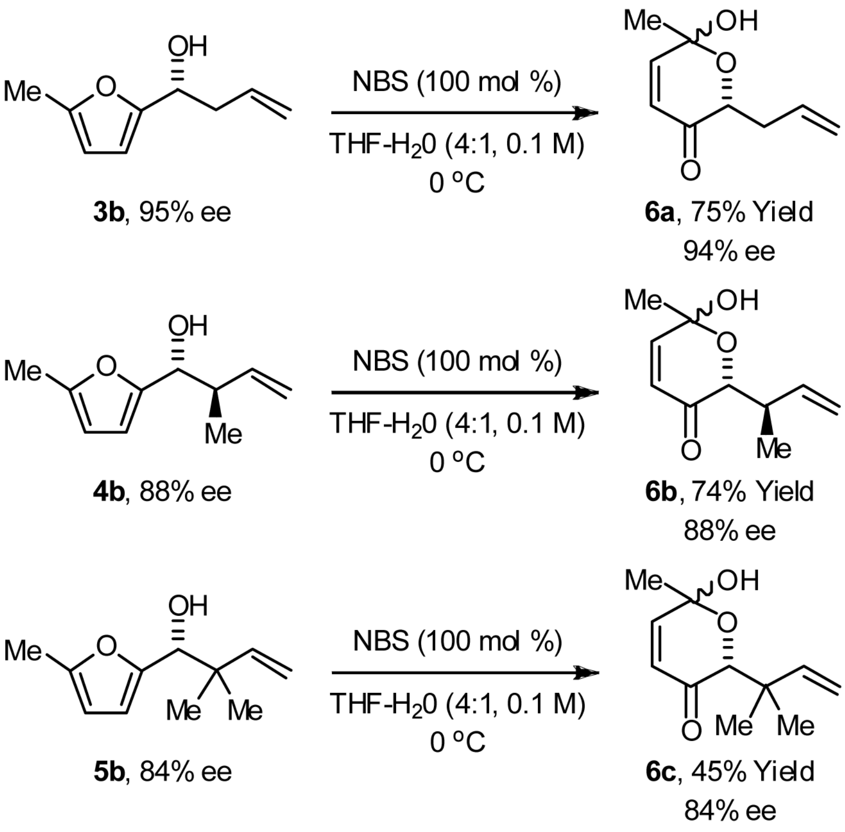
References

1. For selected reviews on C-C bond forming hydrogenation and transfer hydrogenation, see: (a) Ngai MY, Kong JR, Krische MJ. J Org Chem 2007;72:1063. [PubMed: 17288361] (b) Skucas E, Ngai MY, Komanduri V, Krische MJ. Acc Chem Res 2007;40:1394. [PubMed: 17784728] (c) Shibahara F, Krische MJ. Chem Lett 2008;37:1102. (d) Bower JF, Kim IS, Patman RL, Krische MJ. Angew Chem Int Ed 2009;48:34. (e) Han SB, Kim IS, Krische MJ. Chem Commun 2009:7278.
2. For enantioselective carbonyl allylation, crotylation and reverse prenylation via iridium catalyzed C-C bond forming transfer hydrogenation, see: (a) Kim IS, Ngai MY, Krische MJ. J Am Chem Soc 2008;130:6340. [PubMed: 18444616] (b) Kim IS, Ngai MY, Krische MJ. J Am Chem Soc 2008;130:14891. [PubMed: 18841896] (c) Kim IS, Han SB, Krische MJ. J Am Chem Soc 2009;131:2514. [PubMed: 19191498] (d) Han SB, Kim IS, Han H, Krische MJ. J Am Chem Soc 2009;131:6916. [PubMed: 19453190] (e) Lu Y, Kim IS, Hassan A, Del Valle DJ, Krische MJ. Angew Chem Int Ed 2009;48:5018. (f) Itoh J, Han SB, Krische MJ. Angew Chem Int Ed 2009;48:6316. (g) Lu Y, Krische MJ. Org Lett 2009;11:3108. [PubMed: 19586066] (h) Hassan A, Lu Y, Krische MJ. Org Lett 2009;11:3112. [PubMed: 19586067] For a recent application in natural product synthesis, see: (i) Harsh P, O’Doherty GA. Tetrahedron 2009;65:5051. [PubMed: 20161297]
3. For selected reviews on enantioselective carbonyl allylation, see: (a) Yamamoto Y, Asao N. Chem Rev 1993;93:2207. (b) Ramachandran PV. Aldrichim Acta 2002;35:23. (c) Kennedy JWJ, Hall DG. Angew Chem Int Ed 2003;42:4732. (d) Denmark SE, Fu J. Chem Rev 2003;103:2763. [PubMed: 12914480] (e) Yu CM, Youn J, Jung HK. Bull Korean Chem Soc 2006;27:463. (f) Marek I, Sklute G. Chem Commun 2007:1683. (g) Hall DG. Synlett 2007:1644.
4. For selected reviews of carbonyl allylation based on the reductive coupling of metallo-π-allyls derived from allylic alcohols, ethers or carboxylates, see: (a) Masuyama, Y. Palladium-Catalyzed Carbonyl Allylation via π-Allylpalladium Complexes. In: Liebeskind, LS., editor. Advances in Metal-Organic Chemistry. Vol. 3. JAI Press; Greenwich: 1994. p. 255-303.(b) Tamaru, Y. Palladium-Catalyzed Reactions of Allyl and Related Derivatives with Organoelectrophiles. In: Negishi, E-i; de Meijere, A., editors. Handbook of Organopalladium Chemistry for Organic Synthesis. Vol. 2. Wiley; New York: 2002. p. 1917-1943.(c) Tamaru, Y. Novel Catalytic Reactions involving π-Allylpalladium and -Nickel as the Key Intermediates: Umpolung and β-Decarbopalladation of π-Allylpalladium and Nickel-Catalyzed Homoallylation of Carbonyl Compounds with 1,3-Dienes. In: Tsuji, J., editor. Perspectives in Organopalladium Chemistry for the XXI Century. Elsevier; Amsterdam: 1999. p. 215-231. (d) Kondo T, Mitsudo T-a. Curr Org Chem 2002;6:1163. (e) Tamaru Y. Eur J Org Chem 2005;13:2647. (f) Zanoni G, Pontiroli A, Marchetti A, Vidari G. Eur J Org Chem 2007;22:3599.
5. For selected examples of carbonyl allylation via catalytic Nozaki-Hiyama-Kishi coupling of allylic halides, see: (a) Fürstner A, Shi N. J Am Chem Soc 1996;118:2533. (b) Bandini M, Cozzi PG, Umani-Ronchi A. Polyhedron 2000;19:537. (c) McManus HA, Cozzi PG, Guiry PJ. Adv Synth Catal 2006;348:551. (d) Hargaden GC, Müller-Bunz H, Guiry PJ. Eur J Org Chem 2007:4235. (e) Hargaden GC, O’Sullivan TP, Guiry PJ. Org Biomol Chem 2008;6:562. [PubMed: 18219428]
6. Kunze B, Jansen R, Hofle G, Reichenbach H. J Antibiot 2004;57:151. [PubMed: 15112964]
7. For selected examples of enantioselective furfural allylation employing preformed allylmetal reagents, see: (a) Racherla US, Liao Y, Brown HC. J Org Chem 1992;57:6614. (b) Keck GE, Geraci LS. Tetrahedron Lett 1993;34:7827. (c) Yanagisawa A, Nakashima H, Ishiba A, Yamamoto H. J Am Chem Soc 1996;118:4723. (d) Loh TP, Zhou JR. Tetrahedron Lett 2000;41:5261. (e) Denmark SE, Wynn T. J Am Chem Soc 2001;123:6199. [PubMed: 11414863] (f) Denmark SE, Fu J. J Am Chem Soc 2001;123:6199. [PubMed: 11414863] (g) Kii S, Maruoka K. Tetrahedron Lett 2001;42:1935. (h) Yanagisawa A, Nakashima H, Nakatsuka Y, Ishiba A, Yamamoto H. Bull Chem Soc Jpn 2001;74:1129. (i) Hanawa H, Uraguchi D, Konishi S, Hashimoto T, Maruoka K. Chem Eur J 2003;9:4405. (j) Hanawa H, Hashimoto T, Maruoka K. J Am Chem Soc 2003;125:1708. [PubMed: 12580590] (k) Xia G, Shibatomi K, Yamamoto H. Synlett 2004:2437. (k) Kwiatkowski P, Jurczak J. Synlett 2005:227. (l) Kwiatkowski P, Chaladaj W, Jurczak J. Synlett 2005:2301. (m) Kwiatkowski P, Chaladaj W, Jurczak J. Tetrahedron 2006;62:5116. (n) Denmark SE, Fu J, Lawler MJ. J Org Chem 2006;71:1523. [PubMed: 16468801]
8. For selected review articles on the chemistry of furans, see: (a) Lipshutz BH. Chem Rev 1986;86:795. (b) Maier, Martin E. Nachr Chem 1993;41:696. (c) Raczko J, Jurczak J. Stud Nat Prod Chem 1995;16:639. (d) Kappe CO, Murphree SS, Padwa A. Tetrahedron 1997;53:14179. (e) Rassu G,

Zanardi F, Battistini L, Casiraghi G. Chem Soc Rev 2000;29:109. (f) D’Auria M, Emanuele L, Racioppi R, Romaniello G. Curr Org Chem 2003;7:1443. (g) Wright DL. Prog Heterocycl Chem 2005;17:1. (h) Montagnon T, Tofi M, Vassilikogiannakis G. Acc Chem Res 2008;41:1001. [PubMed: 18605738]

9. (a) Achmatowicz O Jr, Bukowski P, Szechner B, Zwierzchowska Z, Zamojski A. Tetrahedron 1971;27:1973.For a review, see: (b) Harris JM, Li M, Scott JG, O’Doherty GA. Strategies Tactics Org Synth 2004;5:221.



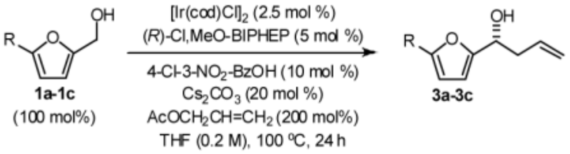
Scheme 1.

Achmatowicz rearrangement of optically enriched adducts **3b**, **4b** and **5b**.[a]

[a]Yields are of material isolated by silica gel chromatography. Enantiomeric excess was determined by chiral stationary phase HPLC analysis.

Table 1

Enantioselective Carbonyl Allylation of Furan Methanols *via* Iridium Catalyzed Transfer Hydrogenation.[a]

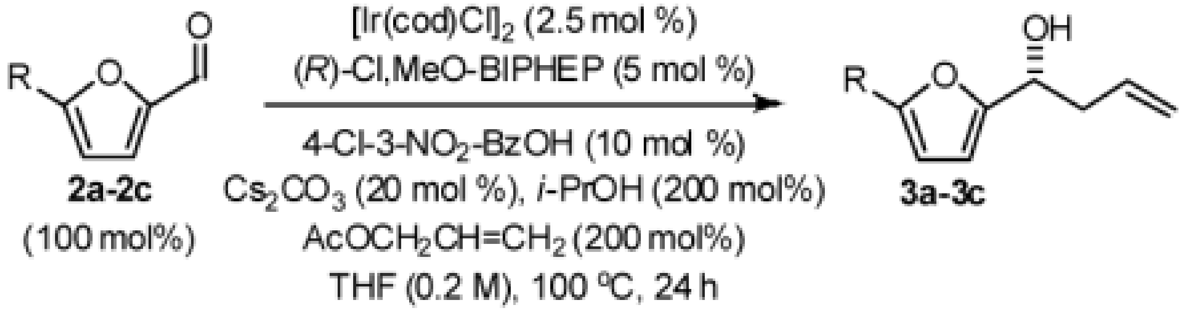


Entry	Furan Methanol	Product	Isolated Yield	ee (%)
1	R = H, **1a**	**3a**	69%	92 (*R*)
2	R = Me, **1b**	**3b**	75%	95 (*R*)
3	R=Ar, **1c**	**3c**	79%	94 (*R*)

[a] Yields are of material isolated by silica gel chromatography. Enantiomeric excess was determined by chiral stationary phase HPLC analysis. For compound **1c**, Ar = 3-chloro-4-methoxyphenyl. See Supporting Information for additional details.

Table 2

Enantioselective Carbonyl Allylation of Furfurals *via* Iridium Catalyzed Transfer Hydrogenation.[a]

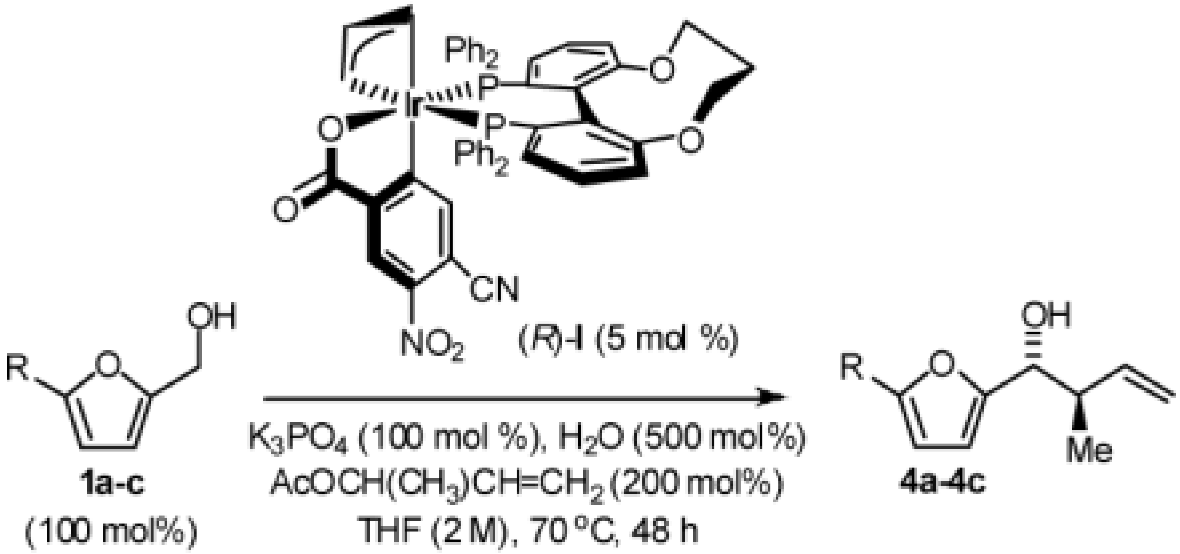


Entry	Furan Methanol	Product	IsolatedYield	ee (%)
1	R = H, **1a**	**3a**	70%	97 (*R*)
2	R = Me, **1b**	**3b**	82%	95 (*R*)
3	R = Ar, **1c**	**3c**	94%	97 (*R*)

[a] As described for Table 1.

Table 3

Enantioselective Carbonyl Crotylation of Furan Methanols *via* Iridium Catalyzed Transfer Hydrogenation.[a]

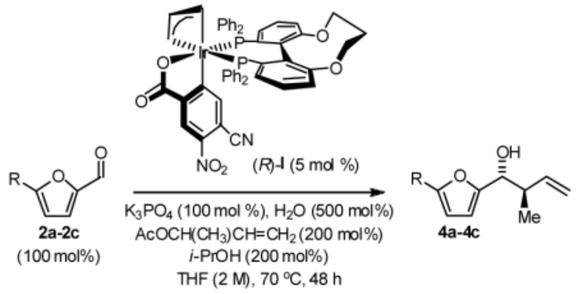


Entry	Furan Methanol	Product	Isolated Yield (dr)	ee (%)
1	R = H, **1a**	**4a**	77%, 10:1	92 (*R*,*R*)
2	R = Me, **1b**	**4b**	76%, 7:1	91 (*R*,*R*)
3	R =Ar, **1c**	**4c**	95%, 10:1	95 (*R*,*R*)

[a] As described for Table 1.

Table 4

Enantioselective Carbonyl Crotylation of Furfurals *via* Iridium Catalyzed Transfer Hydrogenation.[a]

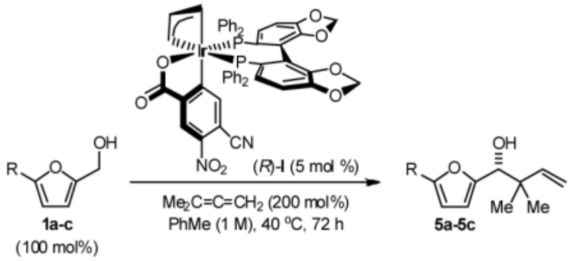


Entry	Furan Methanol	Product	IsolatedYield(dr)	ee (%)
1	R = H, **1a**	**4a**	72%, >20:1	97 (*R*,*R*)
2	R = Me, **1b**	**4b**	79%, >20:1	94 (*R*,*R*)
3	R = Ar, **1c**	**4c**	94%, >20:1	99 (*R*,*R*)

[a] As described for Table 1.

Table 5

Enantioselective Carbonyl *tert*-Prenylation Furan Methanols *via* Iridium Catalyzed Transfer Hydrogenation.[a]

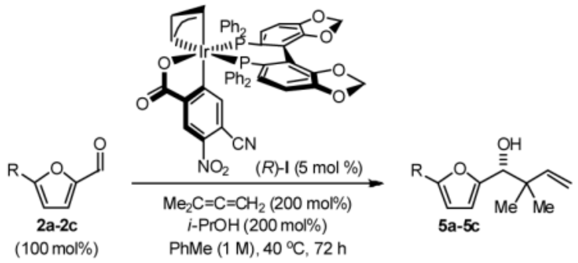


Entry	Furan Methanol	Product	Isolated Yield	ee (%)
1	R = H, **1a**	**5a**	82%	87 (*R*)
2	R = Me, **1b**	**5b**	84%	84 (*R*)
3	R=Ar, **1c**	**5c**	91%	85 (*R*)

[a] As described for Table 1.

Table 6

Enantioselective Carbonyl *tert*-Prenylation of Furfurals *via* Iridium Catalyzed Transfer Hydrogenation.[a]



Entry	Furan Methanol	Product	IsolatedYield	ee (%)
1	R = H, **1a**	**5a**	82%	88 (*R*)
2	R = Me **1b**	**5b**	89%	89 (*R*)
3	R = Ar, **1c**	**5c**	94%	93 (*R*)

[a] As described for Table 1.