Tetrahedron xxx (2015) 1–7

Contents lists available at ScienceDirect

Tetrahedron

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

Fe(OTf)$_3$-mediated synthesis of sulfonyl dihydropyrans

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ARTICLE INFO

Article history:
Received 15 October 2015
Received in revised form 24 November 2015
Accepted 2 December 2015
Available online xxx

Keywords:
Sulfonyl dihydrofurans
β-Ketosulfones
Prenyl alcohol

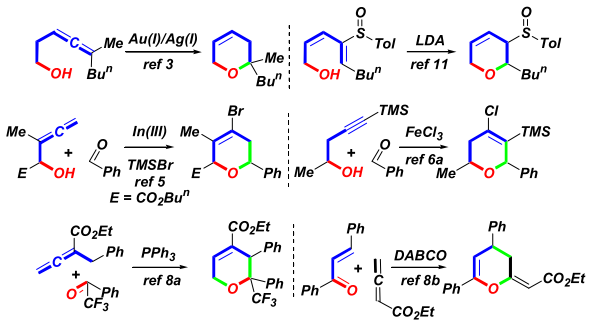
ABSTRACT

Fe(OTf)$_3$-mediated one-pot (3+3) cycloaddition of β-ketosulfones **1** with prenyl alcohol (**2**) in $MeNO_2$ affords sulfonyl dihydropyrans **5** in good yields via a sequential intermolecular α-prenylation followed by intramolecular Friedel–Crafts alkylation. The method provides a highly effective condition.

1. Introduction

Functionalized oxygen-containing heterocycles are key core structures of many natural products and biologically active molecules.[1] Among these diversified building blocks, dihydropyrans and their derivatives can be widely found from natural sources, including FR 1828277,[2a] plumisclerin A,[2b] acuminolide A,[2c] penostatin B[2d] and iridoid alkaloids.[2e] For various protocols on the synthesis of dihydropyrans, transition-metal complexes (Au/Ag,[3] Bi,[4] In,[5] Fe,[6] Pd,[7] Ru,[8] Zn[9]) promoting cycloisomerization of allenols or alkynols are the major pathways. Synthetic routes to organocatalysts mediated cyclization of allenoate with enones or ketones have been documented.[10,11] Based on these observations,[12] we found that an intramolecular base-mediated ring-closure, an intermolecular (4+2) annulation or a Prins-type (5+1) cyclization provide some dominant accesses to substituted dihydropyrans among these methodologies (see Scheme 1). To the best of our knowledge, for the synthesis of sulfonyl dihydropyrans, no examples of a one-pot (3+3) annulation of β-ketosulfones with prenyl alcohol has been reported.

Notably, few reports have been presented for generating 3-sulfonyl dihydropyrans. For example, Pradilla developed base-promoted intramolecular S_N2' cyclization of sulfinyl dienols followed by oxidation of the corresponding allylic sulfinyl dihydropyrans.[11] However, new synthetic designs of sulfone-based



Scheme 1. Synthetic routes of substituted dihydrofurans.

dihydropyrans still represent a continuing need in the organic field, especially those that allow one-pot tandem operations. In continuation of our investigation into the synthetic application of β-ketosulfones,[13,14] Fe(OTf)$_3$ (**3c**) mediated synthesis of 3-sulfonyl dihydropyrans with a germinal 2,2-dimethyl motif is developed, including (i) an intermolecular α-prenylation of β-ketosulfones **1** with a prenyl alcohol (**2**) and (ii) an intramolecular Friedel–Crafts alkylation of the resulting α-prenyl-β-ketosulfones **4** (see Scheme 2). Noviose (a sugar component of novabiocin) also possesses a germinal 2,2-dimethyl substituent.[15] Herein, we describe a highly effective synthesis of dihydropyrans **5** bearing a rigid conformer of (2*E*)-β-oxyvinyl sulfone with an electronic 'push–pull' characteristic by formal (3+3) cycloaddition.

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http://dx.doi.org/10.1016/j.tet.2015.12.007
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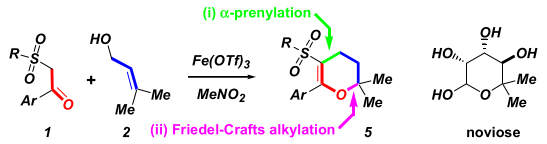
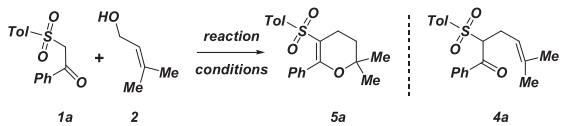


Scheme 2. Our synthetic route of **5**.

2. Results and discussion

To design sulfonyl noviose analogues, we utilize the prenyl group as the three-carbon synthon and source of a germinal dimethyl group. According to previous literature on the direct alkylation of active methylenes with a cinnamyl or benzyl alcohols, metal complex-mediated carbon–carbon bond formation has been developed by Rueping[16a] and Baba[16b] via $Bi(OTf)_3$ or $InCl_3$ promoted α-conjugation of 1,3-dicarbonyl synthons with alcohols. With this idea in mind, catalytic amounts (1, 3 or 10 mol %) of $Bi(OTf)_3$ (**3a**) and $InCl_3$ (**3b**) were first examined for the α-prenylation of model substrate **3a** (R=Tol, Ar=Ph) with prenyl alcohol in $MeNO_2$ at 25 °C for 20 h. However, attempts to afford this alkylated adduct **4a** were unsuccessful, as shown in Table 1 (entries 1–6). To elevate the temperature (25 → 100), the desired **5a** was only isolated in low yield (<20%). When 3 mol % of $Fe(OTf)_3$ (**3c**) served as the catalyst (entries 7–11), **5a** was isolated in a higher (79%) yield in boiling $MeNO_2$ after 20 h. Among metal triflate derivatives, $Fe(OTf)_3$ belongs to the most relative and used catalyst comparable to other Lewis acids, such as $Sc(OTf)_3$, $Yb(OTf)_3$, AgOTf, and $In(OTf)_3$. For the Fe(III) complex (entry 12), $FeCl_3$ (**3d**) produced **5a** in a 58% yield along with an 18% of complex mixture. As shown in entries 13–14, Bronsted acids, such as *p*-TsOH (**3e**) and TFA (**3f**), don't show catalytic activity. On the basis of a higher yield and activity, we believe that 3 mol % of $Fe(OTf)_3$ (**3c**)/$MeNO_2$/reflux reaction condition should be an optimal combination (entry 8) for examining the formation of skeleton **5**.

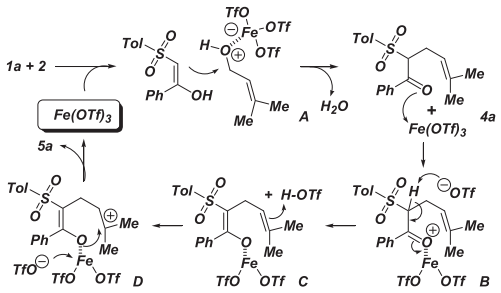
Table 1
One-pot conditions[a]



Entry	3 (mol %), solvent, temp (°C)	**5a**, yield (%)[b]
1	$Bi(OTf)_3$ **3a** (1), $MeNO_2$, 25	—[c]
2	$Bi(OTf)_3$ **3a** (3), $MeNO_2$, 25	—[c]
3	$Bi(OTf)_3$ **3a** (10), $MeNO_2$, 25	—[c]
4	$Bi(OTf)_3$ **3a** (1), $MeNO_2$, 101	10[d]
5	$InCl_3$ **3b** (10), toluene, 25	—[c]
6	$InCl_3$ **3b** (10), toluene, 111	11[e]
7	$Fe(OTf)_3$ **3c** (3), $MeNO_2$, 25	32[f]
8	$Fe(OTf)_3$ **3c** (3), $MeNO_2$, 101	79 (75)[g]
9	$Fe(OTf)_3$ **3c** (10), $MeNO_2$, 101	74 (74)[g]
10	$Fe(OTf)_3$ **3c** (3), toluene, 111	70
11	$Fe(OTf)_3$ **3c** (3), 1,4-dioxane, 101	67
12	$FeCl_3$ **3d** (3), $MeNO_2$, 101	58[h]
13	*p*-TsOH **3e** (3), $MeNO_2$, 101	—[c]
14	TFA **3f** (3), $MeNO_2$, 101	—[c]

[a] Reactions were run on a 1.0 mmol scale with **1a**, **2** (1.05 equiv), solvents (5 mL), 20 h.
[b] Isolated yields.
[c] No reaction was observed and major **1a** was recovered.
[d] 30% of 3-methylbiphenyl and ~8% of **4a** were isolated.
[e] 28% of **4a** was isolated and 32% of **1a** was recovered.
[f] 48% of **4a** was isolated.
[g] 40 h.
[h] 18% of complex mixture was isolated.

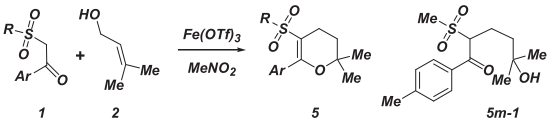
Based on the results, a possible reaction mechanism is shown in Scheme 3. The mechanism should be initiated to form **A** by complexation of a hydroxyl motif of **2** with $Fe(OTf)_3$, and participation of methylene of **1a** could lead to **4a**, removal of H_2O, and the recovery of $Fe(OTf)_3$ via intermolecular alkylation. Furthermore, complexation of **4a** with $Fe(OTf)_3$ should give **B**. Then, deprotonation of **B** by in situ formed triflate anions is produced to the HOTf and an alternative **C** with an iron-chelated enolate. Protonation of **C** with the resulting HOTf affords tertiary carbocation **D**, which, following the loss of $Fe(OTf)_3$, is able to provide **5a** and the recovery of $Fe(OTf)_3$.



Scheme 3. Possible mechanism.

According to the above reaction conditions, we explored the substrate scope, and the results are shown in Table 2. To adjust Ar and R groups of **1a**–**p**, **5a**–**p** (Ar=Ph, 4-FC_6H_4, 4-$MeOC_6H_4$, 4-MeC_6H_4, 3-$NO_2C_6H_4$, 4-$CF_3C_6H_4$, 4-PhC_6H_4, 2-naphthalene; R=Tol, Ph, Me, 4-FC_6H_4, 4-$MeOC_6H_4$) were provided, as shown in entries 1–16. For the Ar groups of **1**, the phenyl ring with a strong electron-withdrawing group (e.g., 4-FC_6H_4, 3-$NO_2C_6H_4$ or 4-$CF_3C_6H_4$) provided the desired **5** in good yields, and the phenyl ring, with an electron-neutral substituent (e.g., Ph, 4-MeC_6H_4, 4-PhC_6H_4, 2-naphthalene) also provided modest to good yields. In particular, the phenyl ring with an electron-donating substituent (for **4c**,

Table 2
Synthesis of **5**[a]



Entry	1, Ar=, R=,	**5**, yield (%)[b]
1	**1a**, Ph, Tol	**5a**, 79
2	**1b**, 4-FC_6H_4, Tol	**5b**, 80
3	**1c**, 4-$MeOC_6H_4$, Tol	**5c**,—[c]
4	**1d**, 4-MeC_6H_4, Tol	**5d**, 65
5	**1e**, 3-$NO_2C_6H_4$, Tol	**5e**, 83
6	**1f**, 4-$CF_3C_6H_4$, Tol	**5f**, 85
7	**1g**, 4-PhC_6H_4, Tol	**5g**, 80
8	**1h**, 2-naphthalene, Tol	**5h**, 72
9	**1i**, Ph, Ph	**5i**, 80
10	**1j**, 4-FC_6H_4, Ph	**5j**, 82
11	**1k**, 4-PhC_6H_4, Ph	**5k**, 83
12	**1l**, Ph, Me	**5l**, 76
13	**1m**, 4-MeC_6H_4, Me	**5m**, trace[d]
14	**1n**, 4-PhC_6H_4, Me	**5n**, 83
15	**1o**, Ph, 4-FC_6H_4	**5o**, 82
16	**1p**, Ph, 4-$MeOC_6H_4$	**5p**, 73

[a] The synthesis of **5** was run on a 1.0 mmol scale with **1**, **2** (1.05 equiv), $Fe(OTf)_3$ (**3c**, 3.0 mol %), $MeNO_2$ (5 mL), 20 h, 101 °C.
[b] Isolated yield.
[c] Complex mixture was isolated.
[d] 62% of **5m**–**1** was isolated.

Ar=4-MeOC$_6$H$_4$, R=Tol) produced complex results and no **4c** was formed. However, for the Fe(OTf)$_3$-mediated reaction of **1m** (Ar=4-MeC$_6$H$_4$, R=Me), the desired **5m** was yielded in trace amounts. Furthermore, 62% of **5m**–**1** was isolated as a major product by the following hydrolysis of **5m** (entry 14). The structural frameworks of **5a**, **5e** and **5l** were determined by single-crystal X-ray crystallography (see Figs. 1–3).[17]

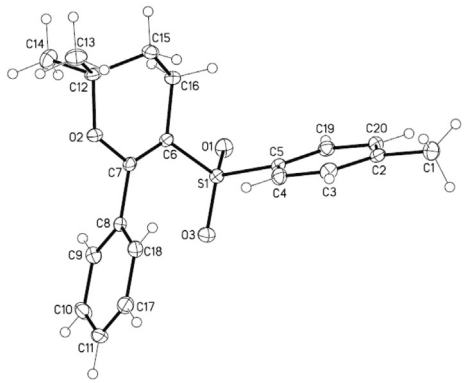


Fig. 1. X-ray structure of **5a**.

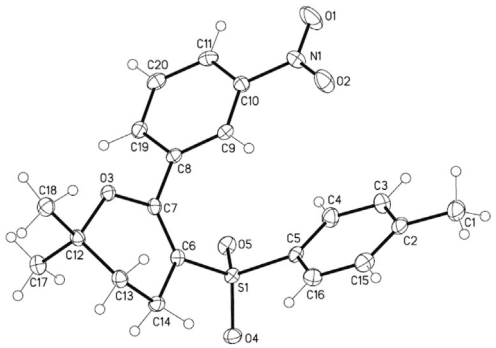


Fig. 2. X-ray structure of **5e**.

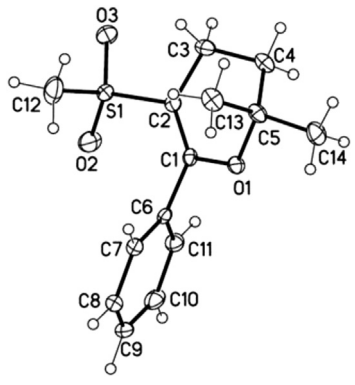
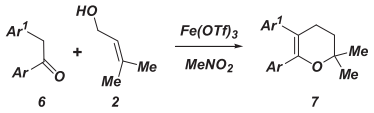


Fig. 3. X-ray structure of **5l**.

Changing the α-substituent from sulfonyl and aryl (Ar^1=Ph, 4-FC$_6$H$_4$, 4-PhC$_6$H$_4$) groups, **7a**–**e** were isolated in yields ranging from 50% to 77% under the one-pot protocol, as shown in Table 3. Interestingly, in comparison to β-ketosulfone **1c**, the phenyl ring of

Table 3
Synthesis of **7**[a]

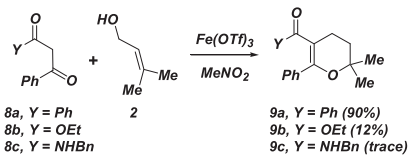


6 2 7

Entry	6, Ar=, Ar^1=,	**7**, yield (%)[b]
1	**6a**, Ph, Ph	**7a**, 70
2	**6b**, 4-FC$_6$H$_4$, Ph	**7b**, 77
3	**6c**, 4-MeOC$_6$H$_4$, 4-FC$_6$H$_4$	**7c**, 62
4	**6d**, 3,4-(MeO)$_2$C$_6$H$_3$, 4-FC$_6$H$_4$	**7d**, 53
5	**6e**, 4-MeOC$_6$H$_4$, 4-PhC$_6$H$_4$	**7e**, 50

[a] The synthesis of **7** was run on a 1.0 mmol scale with **6**, **2** (1.05 equiv), Fe(OTf)$_3$ (**3c**, 3.0 mol %), MeNO$_2$ (5 mL), 20 h, 101 °C.
[b] Isolated yield.

deoxybenzoin **6c**–**e** with an electron-donating substituent (for **7c** and **7e**, Ar=4-MeOC$_6$H$_4$; for **7d**, Ar=3,4-(MeO)$_2$C$_6$H$_3$) could afford modest yields (50%–63%) by the above conditions (see entries 3–6). In Scheme 4, for the reaction of β-diketone **8a** with Fe(OTf)$_3$, high yields (90%) of **9a** were observed. The structure of **9a** was determined by single-crystal X-ray crystallography (see Fig. 4),[17] but, both β-ketoester **8b** and β-ketoamide **8c** gave complex mixtures under the above conditions, and the desired **9b** and **9c** were isolated in a 12% yield and the trace amounts.



8a, Y = Ph
8b, Y = OEt
8c, Y = NHBn

2

9a, Y = Ph (90%)
9b, Y = OEt (12%)
9c, Y = NHBn (trace)

Scheme 4. Fe(OTf)$_3$ mediated reaction of **8** with **2**.

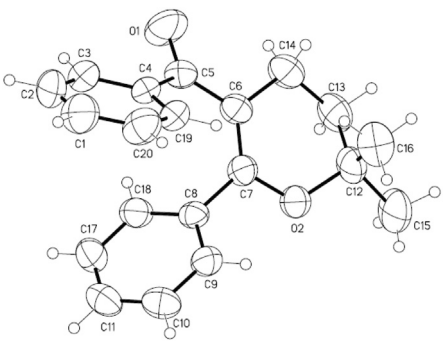
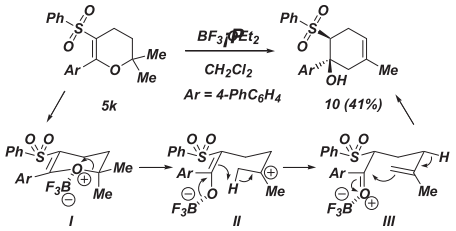


Fig. 4. X-ray structure of **9a**.

Furthermore, treatment of **5k** with BF$_3$·OEt$_2$ (2.0 equiv) afforded a cyclohexenol skeleton **10** in a 41% yield via the transannulation procedure, as shown in Scheme 5. Through the complexation of **5k** with BF$_3$·OEt$_2$, **I** is first formed. By a C–O bond dissociated ring-opening, **I** in situ converts into **II** with a tertiary carbocation. Then, an intramolecular proton change of **II** affords **III**, which, following carbonyl addition of the olefinic motif, is able to provide **10** with a six-membered ring via an intramolecular ring-closure and recovery of BF$_3$·OEt$_2$. A relative stereochemistry of **10** is formed in a *trans*-conformation between biphenyl and sulfonyl substituents. The structure of **10** with the *trans*-diphenyl substituents was determined by single-crystal X-ray crystallography (see Fig. 5).[17]

Please cite this article in press as: Chang, M.-Y.; et al., Tetrahedron (2015), http://dx.doi.org/10.1016/j.tet.2015.12.007



Scheme 5. $BF_3 \cdot OEt_2$-mediated reaction of **5k**.

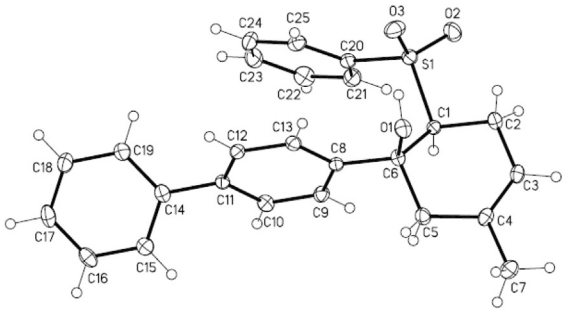
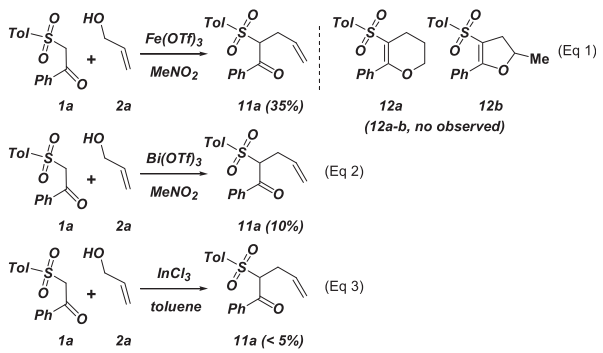


Fig. 5. X-ray structure of **10**.

Following a successful $Fe(OTf)_3$-mediated one-pot (3+3) cycloaddition of β-ketosulfones **1** with prenyl alcohol (**2**), we decided to examine allyl alcohol (**2a**) as the electrophile in the reaction (see Scheme 6). Changing an internal alkene (prenyl alcohol **2**) to a terminal alkene (allyl alcohol **2a**), only 35% of **11a** was generated along with 43% yield of **1a** (Eq. 1). Under the standard conditions, no isolation of cyclized products (dihydropyran **12a** and dihyrdofuran **12b**) was observed. According to the above observations, we envisioned that prenyl alcohol (**2**) is better electrophile than allyl alcohol (**2a**) for one pot (3+3) ring-closure of β-ketosulfone **1a**. To adjust the reaction combination from $Fe(OTf)_3/MeNO_2$ to $Bi(OTf)_3/MeNO_2$ (Table 1, entry 4)[16a] or $InCl_3$/toluene (Table 1, entry 6),[16b] **11a** was generated in low yield (10% or<5%) and **1a** (78% or 90%) was recovered as the major products (Eqs. 2–3). Compared with three catalysts-mediated reaction of **1a** with **2a**, we found that $Fe(OTf)_3$ afforded **11a** in a better yield (35%) than $Bi(OTf)_3$ and $InCl_3$.



Scheme 6. Reaction of **1a** with allyl alcohol (**2a**).

3. Conclusion

In summary, we have developed a mild, facile and one-pot synthesis of substituted dihydropyrans **5**, **7** and **9** in moderate to good yields via an $Fe(OTf)_3$-mediated (3+3) cycloaddition of β-ketosulfones **1**, deoxybenzoins **6** and 1,3-dicarbonyl compound **8** with prenyl alcohol (**2**) in $MeNO_2$ under a one-pot process. The plausible mechanism has been discussed and proposed. The structures of the key products were confirmed by X-ray crystallography. Further investigation regarding synthetic applications of β-ketosulfones will be conducted and published in due course.

4. Experimental section

4.1. General

All other reagents and solvents were obtained from commercial sources and used without further purification. Reactions were routinely carried out under an atmosphere of dry nitrogen with magnetic stirring. Products in organic solvents were dried with anhydrous magnesium sulfate before concentration in vacuo. Melting points were determined with a SMP3 melting apparatus. ^1H and ^{13}C NMR spectra were recorded on a Varian INOVA-400 spectrometer operating at 400 and at 100 MHz, respectively. Chemical shifts (δ) are reported in parts per million (ppm) and the coupling constants (J) are given in Hertz. High resolution mass spectra (HRMS) were measured with a mass spectrometer Finnigan/Thermo Quest MAT 95XL. X-ray crystal structures were obtained with an Enraf-Nonius FR-590 diffractometer (CAD4, Kappa CCD).

4.2. A representative synthetic procedure of 5 is as follows

$Fe(OTf)_3$ (**3c**, 15 mg, 0.03 mmol) was added to a solution of β-ketosulfones **1** (1.0 mmol) and prenyl alcohol (**2**, 90 mg, 1.05 mmol) in $MeNO_2$ (5 mL) at 25 °C. The reaction mixture was stirred at 25 °C for 10 min. The reaction mixture was stirred at reflux for 20 h. The reaction mixture was cooled to rt and the solvent was concentrated. The residue was diluted with water (10 mL) and the mixture was extracted with CH_2Cl_2 (3×20 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc=8/1–4/1) afforded **5**.

*4.2.1. 2,2-Dimethyl-6-phenyl-5-(toluene-4-sulfonyl)-3,4-dihydro-2H-pyran (**5a**).* Yield=79% (270 mg); Colorless solid; mp=135–136 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{20}H_{23}O_3S$ 343.1368, found 343.1372; ^1H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, J=8.0 Hz, 2H), 7.38–7.35 (m, 1H), 7.32–7.23 (m, 4H), 7.13 (d, J=8.0 Hz, 2H), 2.54 (t, J=6.8 Hz, 2H), 2.37 (s, 3H), 1.80 (t, J=6.8 Hz, 2H), 1.28 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.07, 142.89, 139.36, 134.79, 129.40 (2×), 129.32, 129.07 (2×), 127.39 (2×), 127.06 (2×), 112.69, 76.75, 32.38, 26.14 (2×), 21.43, 20.62; Anal. Calcd for $C_{20}H_{22}O_3S$: C, 70.15; H, 6.48. Found: C, 70.31; H, 6.35. Single-crystal X-ray diagram: crystal of compound **5a** was grown by slow diffusion of EtOAc into a solution of compound **5a** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group P 21/n, a=11.7068(7) Å, b=6.0607(4) Å, c=24.6616(15) Å, V=1700.18(18) Å^3, Z=4, d_{calcd}=1.338 mg/cm^3, $F(000)$=728, 2θ range 1.700–26.386°, R indices (all data) R1=0.0350, wR2=0.0984.

*4.2.2. 6-(4-Fluorophenyl)-2,2-dimethyl-5-(toluene-4-sulfonyl)-3,4-dihydro-2H-pyran (**5b**).* Yield=80% (288 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{20}H_{22}FO_3S$ 361.1274, found 361.1278; ^1H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, J=8.4 Hz, 2H), 7.25–7.22 (m, 2H), 7.15 (d, J=8.0 Hz, 2H), 7.00–6.96 (m, 2H), 2.52 (t, J=6.8 Hz, 2H), 2.38 (s, 3H), 1.80 (t, J=6.8 Hz, 2H), 1.28 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.39 (d, J=247.9 Hz), 159.99, 143.13, 139.28, 131.56 (d,

J=9.1 Hz, 2×), 129.17 (2×), 129.68, 127.04 (2×), 114.50 (d, J=21.2 Hz, 2×), 113.12, 76.68, 32.37, 26.14 (2×), 21.47, 20.72.

*4.2.3. 2,2-Dimethyl-5-(toluene-4-sulfonyl)-6-p-tolyl-3,4-dihydro-2H-pyran (**5d**).* Yield=65% (231 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{21}H_{25}O_3S$ 357.1524, found 357.1523; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (d, J=8.4 Hz, 2H), 7.17–7.10 (m, 6H), 2.50 (t, J=6.8 Hz, 2H), 2.38 (s, 3H), 2.36 (s, 3H), 1.79 (t, J=6.8 Hz, 2H), 1.27 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.28, 142.89, 139.49, 139.46, 132.05, 129.34 (2×), 129.08 (2×), 128.15 (2×), 127.16 (2×), 112.24, 76.68, 32.44, 26.18 (2×), 21.48, 21.45, 20.72.

*4.2.4. 2,2-Dimethyl-6-(3-nitrophenyl)-5-(toluene-4-sulfonyl)-3,4-dihydro-2H-pyran (**5e**).* Yield=83% (321 mg); Colorless solid; mp=148–149 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{20}H_{22}NO_5S$ 388.1219, found 388.1222; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (ddd, J=1.2, 2.4, 8.4 Hz, 1H), 7.95 (t, J=2.4 Hz, 1H), 7.71 (dt, J=1.2, 8.4 Hz, 1H), 7.53 (t, J=8.0 Hz, 1H), 7.43 (d, J=8.4 Hz, 2H), 7.20 (d, J=8.0 Hz, 2H), 2.51 (t, J=6.8 Hz, 2H), 2.37 (s, 3H), 1.81 (t, J=6.8 Hz, 2H), 1.30 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.05, 143.72, 138.65, 136.38, 135.95, 129.52, 129.45 (2×), 128.46, 127.00 (2×), 124.05, 124.04, 114.13, 77.64, 32.13, 26.09 (2×), 21.38, 20.44; Anal. Calcd for $C_{20}H_{21}NO_5S$: C, 62.00; H, 6.46. Found: C, 62.21; H, 6.68. Single-crystal X-ray diagram: crystal of compound **5e** was grown by slow diffusion of EtOAc into a solution of compound **5e** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the triclinic crystal system, space group P-1, a=9.0782(4) Å, b=9.6023(5) Å, c=11.7138(6) Å, V=915.61(8) Å^3, Z=2, d_{calcd}=1.405 mg/cm^3, F(000)=408, 2θ range 1.829–26.468°, R indices (all data) R1=0.0401, wR2=0.0839.

*4.2.5. 2,2-Dimethyl-5-(toluene-4-sulfonyl)-6-(4-trifluoromethylphenyl)-3,4-dihydro-2H-pyran (**5f**).* Yield=85% (349 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{21}H_{22}F_3O_3S$ 411.1242, found 411.1245; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, J=8.0 Hz, 2H), 7.41 (d, J=8.4 Hz, 2H), 7.38 (d, J=8.0 Hz, 2H), 7.16 (d, J=8.0 Hz, 2H), 2.52 (t, J=6.8 Hz, 2H), 2.37 (s, 3H), 1.81 (t, J=6.8 Hz, 2H), 1.29 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.24, 143.38, 138.84, 138.39, 131.29, 130.97, 129.82 (2×), 129.26 (2×), 124.43 (d, J=3.8 Hz, 2×), 124.35 (d, J=3.8 Hz, 2×), 113.67, 77.26, 32.20, 26.10 (2×), 21.40, 20.45; Anal. Calcd for $C_{21}H_{21}F_3O_3S$: C, 61.45; H, 5.16. Found: C, 61.78; H, 5.31.

*4.2.6. 6-Biphenyl-4-yl-2,2-dimethyl-5-(toluene-4-sulfonyl)-3,4-dihydro-2H-pyran (**5g**).* Yield=80% (334 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{26}H_{27}O_3S$ 419.1681, found 419.1687; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61–7.59 (m, 2H), 7.54–7.43 (m, 6H), 7.39–7.33 (m, 3H), 7.14 (d, J=8.0 Hz, 2H), 2.57 (t, J=6.8 Hz, 2H), 2.37 (s, 3H), 1.83 (t, J=6.8 Hz, 2H), 1.31 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.76, 142.96, 142.24, 140.62, 133.68, 129.93 (2×), 129.70, 129.07 (2×), 128.75 (2×), 127.52, 127.16 (2×), 127.14 (2×), 126.17 (2×), 112.94, 77.32, 32.40, 26.17 (2×), 21.46, 20.68.

*4.2.7. 2,2-Dimethyl-6-naphthalen-2-yl-5-(toluene-4-sulfonyl)-3,4-dihydro-2H-pyran (**5h**).* Yield=72% (282 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{24}H_{25}O_3S$ 393.1524, found 393.1520; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84–7.76 (m, 2H), 7.74 (d, J=8.4 Hz, 1H), 7.70 (s, 1H), 7.53–7.47 (m, 2H), 7.34 (d, J=8.4 Hz, 2H), 7.29 (dd, J=1.6, 8.4 Hz, 1H), 7.02 (d, J=8.0 Hz, 2H), 2.62 (t, J=6.8 Hz, 2H), 2.31 (s, 3H), 1.86 (t, J=6.8 Hz, 2H), 1.33 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.03, 142.94, 139.44, 133.55, 132.28, 132.09, 129.41, 128.99 (2×), 128.40, 127.65, 127.12 (2×), 127.08, 126.78, 126.45, 126.13, 113.39, 76.92, 32.50, 26.20 (2×), 21.39, 20.73.

*4.2.8. 5-Benzenesulfonyl-2,2-dimethyl-6-phenyl-3,4-dihydro-2H-pyran (**5i**).* Yield=80% (262 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{19}H_{21}O_3S$ 329.1212, found 329.1214; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52–7.43 (m, 3H), 7.38–7.21 (m, 7H), 2.57 (t, J=6.8 Hz, 2H), 1.82 (t, J=6.8 Hz, 2H), 1.29 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.49, 142.28, 134.63, 132.17, 129.43 (2×), 129.39, 128.44 (2×), 127.45 (2×), 126.98 (2×), 112.56, 76.88, 32.38, 26.14 (2×), 20.64.

*4.2.9. 5-Benzenesulfonyl-6-(4-fluorophenyl)-2,2-dimethyl-3,4-dihydro-2H-pyran (**5j**).* Yield=82% (284 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{19}H_{20}FO_3S$ 347.1117, found 347.1121; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53–7.44 (m, 3H), 7.37–7.33 (m, 2H), 7.25–7.20 (m, 2H), 7.00–6.94 (m, 2H), 2.54 (t, J=6.8 Hz, 2H), 1.80 (t, J=6.8 Hz, 2H), 1.27 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.31 (d, J=247.8 Hz), 160.31, 142.10, 132.31, 131.52 (d, J=8.3 Hz, 2×), 130.62 (d, J=3.1 Hz), 128.49 (2×), 126.84 (2×), 114.46 (d, J=22.0 Hz, 2×), 112.87, 77.00, 32.26, 26.04 (2×), 20.63; Anal. Calcd for $C_{19}H_{19}FO_3S$: C, 65.88; H, 5.53. Found: C, 66.07; H, 5.68.

*4.2.10. 5-Benzenesulfonyl-6-biphenyl-4-yl-2,2-dimethyl-3,4-dihydro-2H-pyran (**5k**).* Yield=83% (335 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{25}H_{25}O_3S$ 405.1524, found 405.1529; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61–7.43 (m, 10H), 7.39–7.28 (m, 4H), 2.61 (t, J=6.8 Hz, 2H), 1.84 (t, J=6.8 Hz, 2H), 1.32 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.13, 142.22, 140.50, 133.46, 132.16, 129.92 (2×), 129.62, 128.81 (2×), 128.39 (2×), 127.52, 127.10 (2×), 126.99 (2×), 126.16 (2×), 112.82, 76.92, 32.35, 26.11 (2×), 20.63.

*4.2.11. 5-Methanesulfonyl-2,2-dimethyl-6-phenyl-3,4-dihydro-2H-pyran (**5l**).* Yield=76% (202 mg); Colorless solid; mp=99–100 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{14}H_{19}O_3S$ 267.1055, found 267.1057; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44–7.36 (m, 5H), 2.65 (s, 3H), 2.60 (t, J=6.8 Hz, 2H), 1.86 (t, J=6.8 Hz, 2H), 1.37 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.75, 134.71, 129.82, 129.28 (2×), 127.93 (2×), 112.56, 77.32, 43.18, 32.36, 26.17 (2×), 20.25. Single-crystal X-ray diagram: crystal of compound **5l** was grown by slow diffusion of EtOAc into a solution of compound **5l** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group P 21/c, a=12.3042(8) Å, b=29.754(2) Å, c=11.0845(7) Å, V=4055.4(5) Å^3, Z=12, d_{calcd}=1.309 mg/cm^3, F(000)=1704, 2θ range 1.369–26.386°, R indices (all data) R1=0.0509, wR2=0.1159.

*4.2.12. 5-Hydroxy-2-methanesulfonyl-5-methyl-1-p-tolyl-hexan-1-one (**5m–1**).* Yield=62% (185 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{15}H_{23}O_5S$ 299.1317, found 299.1319; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, J=8.4 Hz, 2H), 7.31 (d, J=7.6 Hz, 2H), 4.98 (dd, J=5.6, 8.8 Hz, 1H), 2.94 (s, 3H), 2.42 (s, 3H), 2.38–2.31 (m, 2H), 1.73 (s, 1H), 1.54–1.47 (m, 1H), 1.42–1.35 (m, 1H), 1.21 (s, 3H), 1.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.45, 145.75, 134.31, 129.65 (2×), 129.38 (2×), 70.38, 68.66, 40.11, 37.24, 29.46, 29.02, 23.98, 21.72.

*4.2.13. 6-Biphenyl-4-yl-5-methanesulfonyl-2,2-dimethyl-3,4-dihydro-2H-pyran (**5n**).* Yield=83% (284 mg); Colorless solid; mp=173–174 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{20}H_{23}O_3S$ 343.1368, found 343.1371; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65–7.59 (m, 4H), 7.54–7.51 (m, 2H), 7.47–7.42 (m, 2H), 7.39–7.34 (m, 1H), 2.72 (s, 3H), 2.64 (t, J=6.8 Hz, 2H), 1.89 (t, J=6.8 Hz, 2H), 1.41 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.46, 142.59, 140.24, 133.53, 129.72 (2×), 128.75 (2×), 127.65, 127.14 (2×), 126.58 (2×), 112.55, 77.03, 43.17, 32.30, 26.16 (2×), 20.30.

*4.2.14. 5-(4-Fluorobenzenesulfonyl)-2,2-dimethyl-6-phenyl-3,4-dihydro-2H-pyran (**5o**).* Yield=82% (284 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{19}H_{20}FO_3S$ 347.1117, found 347.1124; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49–7.44 (m, 2H), 7.39–7.34 (m, 1H),

7.31–7.26 (m, 2H), 7.23–7.20 (m, 2H), 7.01–6.96 (m, 2H), 2.57 (t, J=6.8 Hz, 2H), 1.82 (t, J=6.8 Hz, 2H), 1.29 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.64 (d, J=253.2 Hz), 161.54, 138.32 (d, J=3.0 Hz), 134.44, 129.61 (d, J=9.1 Hz, 2×), 129.43, 129.37 (2×), 127.43 (2×), 115.52 (d, J=22.0 Hz, 2×), 112.66, 76.91, 32.27, 26.04 (2×), 20.52.

*4.2.15. 5-(4-Methoxybenzenesulfonyl)-2,2-dimethyl-6-phenyl-3,4-dihydro-2H-pyran (**5p**).* Yield=73% (261 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{20}H_{23}O_4S$ 359.1317, found 359.1321; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, J=8.8 Hz, 2H), 7.38–7.23 (m, 5H), 6.79 (d, J=8.8 Hz, 2H), 3.81 (s, 3H), 2.53 (t, J=6.8 Hz, 2H), 1.80 (t, J=6.8 Hz, 2H), 1.28 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.49, 160.73, 134.82, 134.02, 129.40 (2×), 129.27, 129.10 (2×), 127.39 (2×), 113.61 (2×), 113.08, 76.65, 55.46, 32.37, 26.10 (2×), 20.59.

4.3. A representative synthetic procedure of 7 is as follows

$Fe(OTf)_3$ (**3c**, 15 mg, 0.03 mmol) was added to a solution of deoxybenzoins **6** (1.0 mmol) and prenyl alcohol (**2**, 90 mg, 1.05 mmol) in $MeNO_2$ (5 mL) at 25 °C. The reaction mixture was stirred at 25 °C for 10 min. The reaction mixture was stirred at reflux for 20 h. The reaction mixture was cooled to rt and the solvent was concentrated. The residue was diluted with water (10 mL) and the mixture was extracted with CH_2Cl_2 (3×20 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc=8/1–4/1) afforded **7**.

*4.3.1. 2,2-Dimethyl-5,6-diphenyl-3,4-dihydro-2H-pyran (**7a**).* Yield=70% (185 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{19}H_{21}O$ 265.1592, found 265.1599; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21–7.06 (m, 10H), 2.51 (t, J=6.8 Hz, 2H), 1.89 (t, J=6.8 Hz, 2H), 1.43 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.83, 142.06, 137.24, 129.50 (2×), 129.47 (2×), 127.90 (2×), 127.45 (2×), 127.30, 125.56, 110.22, 73.56, 33.59, 26.34 (2×), 25.75.

*4.3.2. 6-(4-Fluorophenyl)-2,2-dimethyl-5-phenyl-3,4-dihydro-2H-pyran (**7b**).* Yield=77% (217 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{19}H_{20}FO$ 283.1498, found 283.1502; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20–7.09 (m, 5H), 7.08–7.05 (m, 2H), 6.85–6.79 (m, 2H), 2.50 (t, J=6.8 Hz, 2H), 1.89 (t, J=6.8 Hz, 2H), 1.43 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.95 (d, J=245.6 Hz), 146.83, 141.85, 133.26 (d, J=3.0 Hz), 131.16 (d, J=7.6 Hz, 2×), 129.47 (2×), 128.02 (2×), 125.70, 114.36 (d, J=21.2 Hz, 2×), 110.32, 73.71, 33.53, 26.30 (2×), 25.73; Anal. Calcd for $C_{19}H_{19}FO$: C, 80.82; H, 6.78. Found: C, 80.68; H, 6.82.

*4.3.3. 5-(4-Fluorophenyl)-6-(4-methoxyphenyl)-2,2-dimethyl-3,4-dihydro-2H-pyran (**7c**).* Yield=62% (193 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{20}H_{22}FO_2$ 313.1604, found 313.1608; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.09 (d, J=9.2 Hz, 2H), 7.03–6.99 (m, 2H), 6.86–6.82 (m, 2H), 6.67 (d, J=8.8 Hz, 2H), 3.74 (s, 3H), 2.44 (t, J=6.4 Hz, 2H), 1.86 (t, J=6.4 Hz, 2H), 1.39 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.89 (d, J=242.5 Hz), 158.85, 147.73, 138.20 (d, J=3.8 Hz), 130.86 (d, J=7.6 Hz, 2×), 130.65 (2×), 129.58, 114.76 (d, J=20.4 Hz, 2×), 112.98 (2×), 108.13, 73.55, 55.12, 33.59, 26.32 (2×), 25.82.

*4.3.4. 6-(3,4-Dimethoxyphenyl)-5-(4-fluorophenyl)-2,2-dimethyl-3,4-dihydro-2H-pyran (**7d**).* Yield=53% (181 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{21}H_{24}FO_3$ 343.1710, found 343.1712; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.04–7.00 (m, 2H), 6.88–6.83 (m, 2H), 6.82 (dd, J=2.0, 8.0 Hz, 1H), 6.67 (d, J=8.4 Hz, 1H), 6.57 (d, J=2.0 Hz, 1H), 3.81 (s, 3H), 3.56 (s, 3H), 2.44 (t, J=6.4 Hz, 2H), 1.86 (t, J=6.4 Hz, 2H), 1.40 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.94 (d, J=242.6 Hz), 148.35, 147.72, 147.63, 138.33, 130.87 (d, J=7.5 Hz, 2×), 129.60, 121.77, 114.82 (d, J=20.4 Hz, 2×), 113.02, 110.30, 108.31, 73.63, 55.73, 55.42, 33.53, 26.31 (2×), 25.89.

*4.3.5. 5-Biphenyl-4-yl-6-(4-methoxyphenyl)-2,2-dimethyl-3,4-dihydro-2H-pyran (**7e**).* Yield=50% (185 mg); Colorless solid; mp=150–151 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{26}H_{27}O_2$ 371.2011, found 371.2013; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58–7.55 (m, 2H), 7.42–7.38 (m, 4H), 7.32–7.28 (m, 1H), 7.17–7.11 (m, 4H), 6.68 (d, J=8.8 Hz, 2H), 3.74 (s, 3H), 2.51 (t, J=6.8 Hz, 2H), 1.88 (t, J=6.8 Hz, 2H), 1.41 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.89, 147.93, 141.38, 140.87, 137.90, 130.75 (2×), 129.78 (2×), 128.66 (2×), 126.94, 126.78 (2×), 126.51 (3×), 113.02 (2×), 108.63, 73.60, 55.14, 33.68, 26.36 (2×), 25.51.

4.4. A representative synthetic procedure of 9 is as follows

$Fe(OTf)_3$ (**3c**, 15 mg, 0.03 mmol) was added to a solution of 1,3-dicarbonyl compounds **8** (1.0 mmol) and prenyl alcohol (**2**, 90 mg, 1.05 mmol) in $MeNO_2$ (5 mL) at 25 °C. The reaction mixture was stirred at 25 °C for 10 min. The reaction mixture was stirred at reflux for 20 h. The reaction mixture was cooled to rt and the solvent was concentrated. The residue was diluted with water (10 mL) and the mixture was extracted with CH_2Cl_2 (3×20 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc=8/1–4/1) afforded **9**.

*4.4.1. (6,6-Dimethyl-2-phenyl-5,6-dihydro-4H-pyran-3-yl)phenylmethanone (**9a**).* Yield=90% (263 mg); Colorless solid; mp=118–119 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{20}H_{21}O_2$ 293.1542, found 293.1544; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, J=7.6 Hz, 2H), 7.20–7.14 (m, 3H), 7.07 (d, J=7.6 Hz, 2H), 7.04–6.98 (m, 3H), 2.67 (t, J=6.8 Hz, 2H), 1.85 (t, J=6.8 Hz, 2H), 1.49 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.83, 159.89, 139.41, 136.16, 131.04, 129.39 (2×), 129.09 (2×), 129.06, 127.52 (2×), 127.49 (2×), 110.73, 75.92, 32.32, 26.24 (2×), 21.63; Anal. Calcd for $C_{20}H_{20}O_2$: C, 82.16; H, 6.89. Found: C, 82.23; H, 7.03. Single-crystal X-ray diagram: crystal of compound **9a** was grown by slow diffusion of EtOAc into a solution of compound **9a** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group P 21, a=6.7885(14) Å, b=15.896(3) Å, c=7.7042(16) Å, V=826.3(3) Å^3, Z=2, d_{calcd}=1.175 mg/cm^3, F(000)=312, 2θ range 2.563–26.465°, R indices (all data) R1=0.0668, wR2=0.1115.

*4.4.2. 6,6-Dimethyl-2-phenyl-5,6-dihydro-4H-pyran-3-carboxylic acid ethyl ester (**9b**).* Yield=12% (31 mg); Colorless gum; HRMS (ESI, M^++1) calcd for $C_{16}H_{21}O_3$ 261.1491, found 261.1490; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50–7.45 (m, 1H), 7.36–7.29 (m, 4H), 3.92 (q, J=7.2 Hz, 2H), 2.49 (t, J=6.8 Hz, 2H), 1.76 (t, J=6.8 Hz, 2H), 1.36 (s, 3H), 1.34 (s, 3H), 1.27 (t, J=8.8 Hz, 1H), 0.91 (t, J=7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.69, 161.96, 137.70, 128.52, 128.40 (2×), 127.52 (2×), 101.83, 76.14, 59.56, 45.94, 32.19, 26.29, 20.17, 13.63.

4.5. 6-Benzenesulfonyl-1-biphenyl-4-yl-3-methyl-cyclohex-3-enol (10)

$BF_3{\cdot}OEt_2$ (57 mg, 0.4 mmol) was added to a solution of **5k** (81 mg, 0.2 mmol) in CH_2Cl_2 (5 mL) at 25 °C. The reaction mixture was stirred at 25 °C for 20 h. The reaction mixture was concentrated and the residue was diluted with water (10 mL) and the mixture was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc=5/1–3/1) afforded **10**. Yield=41% (34 mg);

Please cite this article in press as: Chang, M.-Y.; et al., Tetrahedron (2015), http://dx.doi.org/10.1016/j.tet.2015.12.007

Colorless solid; mp=164–165 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{25}H_{25}O_3S$ 405.1524, found 405.1532; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50–7.35 (m, 6H), 7.30–7.27 (m, 2H), 7.20–7.13 (m, 6H), 5.60 (br t, J=1.2 Hz, 1H), 4.59 (br s, 1H), 3.97 (dd, J=6.0, 12.0 Hz, 1H), 3.00–2.92 (m, 1H), 2.82–2.74 (m, 1H), 2.43 (d, J=18.0 Hz, 1H), 2.22 (d, J=18.0 Hz, 1H), 1.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.98, 140.46, 140.32, 139.74, 132.37, 132.15, 128.82 (2×), 128.71 (2×), 127.38 (3×), 126.84 (2×), 126.41 (2×), 125.97 (2×), 117.37, 73.32, 65.85, 47.59, 23.00, 22.70. Single-crystal X-ray diagram: crystal of compound **10** was grown by slow diffusion of EtOAc into a solution of compound **10** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group P 21, a=8.8436(5) Å, b=12.7602(8) Å, c=9.6190(6) Å, V=1008.11(11) Å^3, Z=2, d_{calcd}=1.333 mg/cm^3, F(000)=428, 2θ range 2.949–26.391°, R indices (all data) R1=0.0267, wR2=0.0735.

4.6. 1-Phenyl-2-(toluene-4-sulfonyl)pent-4-en-1-one (11a)

$Fe(OTf)_3$ (**3c**, 15 mg, 0.03 mmol) was added to a solution of β-ketosulfone **1a** (274 mg, 1.0 mmol) and allyl alcohol (**2a**, 61 mg, 1.05 mmol) in $MeNO_2$ (5 mL) at 25 °C. The reaction mixture was stirred at 25 °C for 10 min. The reaction mixture was stirred at reflux for 20 h. The reaction mixture was cooled to rt and the solvent was concentrated. The residue was diluted with water (10 mL) and the mixture was extracted with CH_2Cl_2 (3×20 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc=8/1–4/1) afforded **11a**. Yield=35% (110 mg); Colorless solid; mp=109–110 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{18}H_{19}O_3S$ 315.1055, found 315.1061; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94–7.91 (m, 2H), 7.62 (d, J=8.4 Hz, 2H), 7.60–7.56 (m, 1H), 7.47–7.43 (m, 2H), 7.29 (d, J=8.0 Hz, 2H), 5.61–5.50 (m, 1H), 5.10 (dd, J=4.0, 11.2 Hz, 1H), 5.01 (dq, J=1.2, 17.2 Hz, 1H), 4.94 (dq, J=1.2, 17.2 Hz, 1H), 2.86–2.71 (m, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.98, 145.47, 137.14, 133.93, 133.19, 131.91, 129.81 (2×), 129.54 (2×), 129.01 (2×), 128.71 (2×), 118.96, 69.24, 32.41, 21.67.

Acknowledgements

The authors would like to thank the Ministry of Science and Technology of the Republic of China for its financial support (MOST 104-2113-M-037-012).

Supplementary data

Experimental procedure and scanned photocopies of NMR ($CDCl_3$) spectral data were supported. Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2015.12.007.

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