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Synthesis of chalcones and flavanones using Julia–Kocienski olefination

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ABSTRACT

A new application of Julia–Kocienski olefination for the synthesis of chalcones and flavanones has been described. 2-(Benzo[*d*]thiazol-2-ylsulfonyl)-1-phenylethanones have been developed as new reagents for direct Julia–Kocienski olefination with aldehydes in the presence of a base, afforded chalcones in good to excellent yields. Whereas, 2-(benzo[*d*]thiazol-2-ylsulfonyl)-1-(2-hydroxyphenyl)ethanone reacted with the aromatic aldehydes to furnish flavanones in good yields via one-pot intra-molecular cyclization.

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1. Introduction

The carbon–carbon double bonds formation is an important reaction of organic chemistry. Thus, a variety of approaches for the synthesis of olefins have been developed attempting to address their regio and stereochemical demands from time to time.[1] Wittig,[2] Johnson,[3] Peterson,[4] Wadsworth–Emmons,[5] and Julia[6] olefination reactions are the most familiar methods for the synthesis of olefins. Among these methodologies Julia olefination has an important place. The classical Julia[7] olefination is based on a two-step reductive elimination process of β-acyloxy aryl sulfones. The modified Julia[8] reaction also known as Julia–Kocienski olefination, which involves direct coupling of heteroarylsulfones with carbonyl compounds in a single step protocol. Since its discovery, the versatility of Julia reaction has been proved by its application in the synthesis of biologically active natural products[9] and emerging as a powerful tool for the synthesis of olefins. Recently Julia–Kocienski olefination has been utilized for the synthesis of simple olefines,[10,11] alkenyl halides,[12] fluoroalkenoate,[13] methylenation of ketones,[14] vinyl ethers,[15] α,β-unsaturated esters and amides, respectively.[16,17] A careful survey of the literature revealed that Julia–Kocienski olefination has not been applied for the synthesis of α,β-unsaturated ketones.[18] Chalcones belong to flavanoid family, have exhibited an impressive array of biological activities, such as anti-malarial,[19] anti-cancer,[20] anti-tuberculosis,[21] anti-mitotic,[22] cardiovascular,[23] anti-leishmanial.[24] Besides, this conjugated enones system is also a key precursor in the synthesis of many biologically important heterocycles such as benzothiazepine,[26] pyrazolines,[27] 1,4-diketones,[28] and flavones.[29]

Chalcones are generally synthesized by the Claisen–Schmidt reaction but very often reaction led to the complex mixture, which is tedious to separate.[30] Although there are several methods available for the synthesis of chalcones but most of them have some limitation.[31] Recently, Buszek et al. have also reported synthesis of chalcones from *N*-vinlypyridinium tetrafluoroborate salt as new class of electrophilic coupling partner via Suzuki reaction.[32] We wish to report here a new application for Julia–Kocienski olefination via the condensation of new Julia coupling partners with aldehyde for the synthesis of conjugated enones (Fig. 1).

2. Results and discussion

Initially our focus was on to the synthesis of efficient Julia coupling partners. Recently Jùrgensen et al. synthesized β-keto heterocyclic sulfone for the enantioselective conjugate addition to enones via a Smiles rearrangement, which inspired us to evaluate the efficacy of heterocyclic sulfone directly into the Julia–Kocienski reaction for the synthesis of chalcones and flavanones.[33] Therefore, some commonly used starting material such as 2-mercaptobenzothiazole, pyridine-2-thiol, 1-phenyl-1*H*-tetrazole-5-thiol, and 3,5-bis (trifluoromethyl)benzenethiol were converted in to the Julia reagents[34] **1a**–**d** via the reaction of phenacyl bromide, followed by the oxidation with *meta*-chloroperbenzoic acid (*m*-CPBA) (Scheme 1). Heteroaryl-sulfonyl phenylethanones **1a**–**d** were used as coupling reagents for the Julia–Kocienski olefination of aldehydes, resulting in the formation of 1,3-diphenyl-2-propen-1-one **3a**.

In our attempt to find an efficient base for the Julia–Kocienski olefination, benzaldehyde was taken as a model and reacted with different coupling reagents **1a**–**d**. Several bases were used such as DBU, LiHMDS, P_4-*t*-Bu, *t*-BuOK, and DABCO to optimize the reaction

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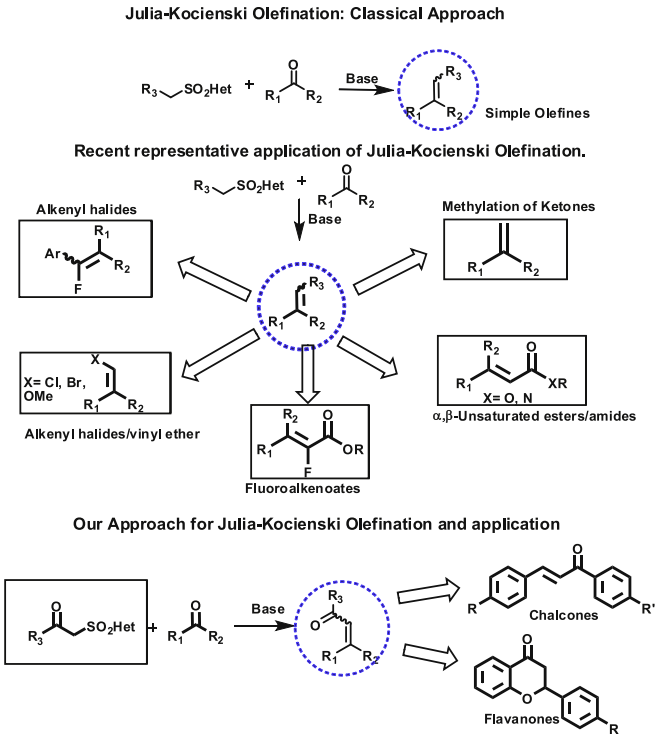
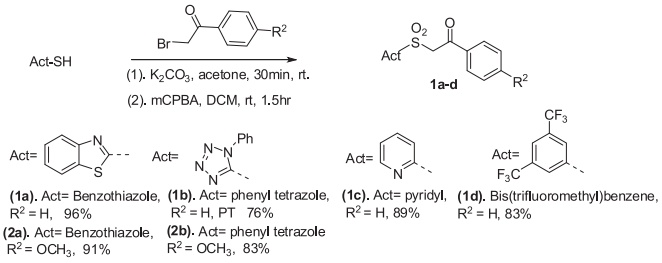


Fig. 1. New application of Julia–Kocienski olefination.



Scheme 1. Synthesis of Julia coupling partners.

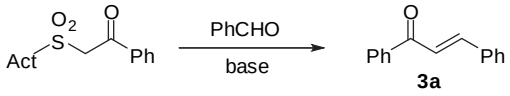
condition. Julia reagent (**1a**) was found to be most efficient Julia coupling reagent from all the coupling reagents (**1a**–**d**) used for the synthesis of conjugated enones in the presence of DBU.

It is noteworthy that Julia activators **1a** and **1b** exhibited better results in comparison to other coupling reagents (**1c**, **1d**) with base such as DBU, LiHMDS, and P_4-*t*-Bu. Whereas, all the used bases such as DBU, LiHMDS, and P_4-*t*-Bu were found unsuitable for the reaction with coupling reagent **1d**. The efficacy of *t*-BuOK and DABCO were not sufficient enough to push the reaction even with **1a**. DBU was found to be most efficient base among all the bases used. The results of coupling reagents and base optimization are summarized in Table 1.

The solvent effect on the Julia coupling of benzaldehyde with coupling partner **1a** was studied and solvents such as DCM, $CHCl_3$, THF, CH_3CN, and methanol were used to optimize the reaction. Non-polar solvents were proved to be better in comparison of polar solvents and the study revealed interesting correlation between solvent polarity and yield (Fig. 2).

To explore the effect of temperature on the selectivity, we carried out reaction of BT-sulfone **1a** and benzaldehyde at −78 °C. No significant effect was observed of low temperature and still the *E* product was the major diastereomer. Reaction yield was also decreased significantly at −78 °C. Formation of anion, which might be

Table 1
Screening of base for the coupling of benzaldehyde and sulfones **1a**–**d**[a]



Entry	Act-	Base	Time/h	Yield[c]	*Z*/*E*[d] (%)
1	**1a**	LiHMDS	14	36	2:98
2	**1b**	LiHMDS	18	23	—
3	**1c**	LiHMDS	18	Trace	—
4	**1d**	LiHMDS	—	—	—
5[b]	**1a**	P_4-*t*-Bu	16	37	5:95
6[b]	**1b**	P_4-*t*-Bu	19	26	—
7[b]	**1c**	P_4-*t*-Bu	19	12	—
8[b]	**1d**	P_4-*t*-Bu	—	—	—
9	**1a**	DBU	16	81	1:99
10	**1b**	DBU	16	79	1:99
11	**1c**	DBU	24	37	—
12	**1d**	DBU	24	<10	—
13	**1a**	*t*-BuOK	—	0	—
14	**1a**	DABCO	—	0	—

[a] Reaction carried out in THF and sulfone (1.8 equiv), and base (1.5 equiv).
[b] Reaction analyzed at 0 °C.
[c] Isolated yields.
[d] Analyzed by ^{1}H NMR.

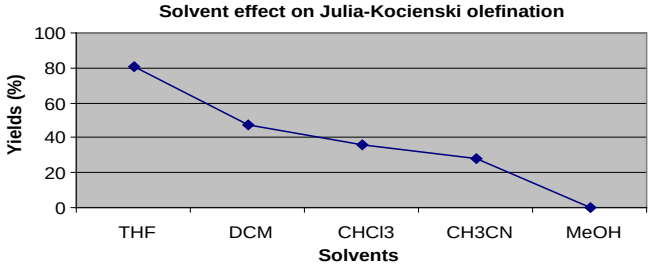
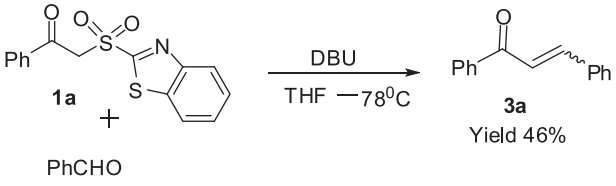


Fig. 2. Solvent effects on Julia olefination.

stabilized by carbonyl group at α-position as well as relatively high stability at lower temperature of the sulfonyl anion limits its reactivity. Thus it can be concluded that modified Julia reaction leads to predominant formation of *E*-chalcones (Scheme 2).

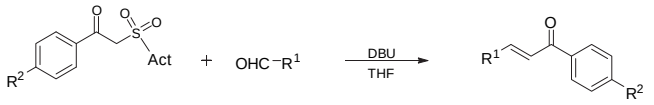


Scheme 2. Effect of the temperature on Julia–Kocienski olefination.

The scope of the modified Julia olefination was examined for the synthesis of series of *E*-enones via the two Julia activators (**1a** and **1b**) (Table 2). The reaction of α-phenacyl sulfones with *O*/*N*-acylated benzaldehyde, and indole-3-carboxaldehyde resulted to the synthesis of functionalized chalcones in high yields. These chalcones are generally not accessible by conventional KOH/NaOH mediated synthesis (Scheme 3).[31]

Recently, Alonso et al. explained the stereoselectivity of olefins interestingly involves enolates. The stereoselectivity of chalcones can be explained by Newman projection (Scheme 4). There are two possible intermediate states (**5a** and **5b**). The Newman projection of the intermediate state **5a** reveals that it is highly unstable due to a steric repulsion between the two aryl groups thus, the

Table 2
DBU mediated synthesis of *E*-enones by the coupling of BT-sulfones and benzaldehyde derivatives in THF[a]



1a, 1b, 2a, 2b

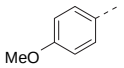
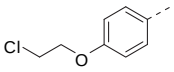
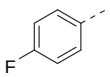
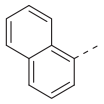
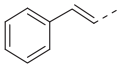
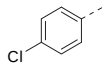
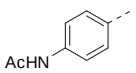
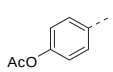
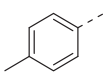
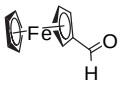
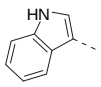
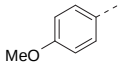
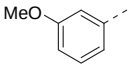
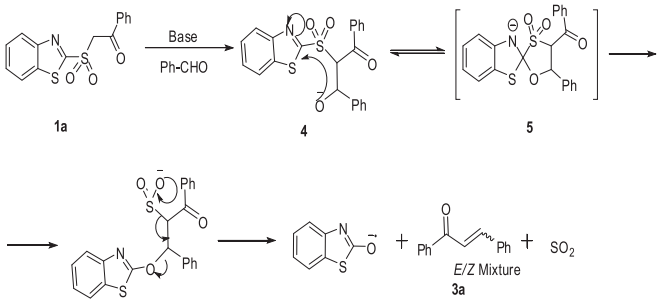
Entry	R^1	Act-	Product[c,d]	Yield[b]
1		**1a**	**3a**	81
2		**1b**	**3a**	74
3		**1a**	**3b**	84
4		**1b**	**3b**	69
5		**1a**	**3c**	86
6		**1b**	**3c**	75
7		**1a**	**3d**	77
8		**1b**	**3d**	59
9		**1a**	**3e**	63
10		**1b**	**3e**	71
11		**1a**	**3f**	88
12		**1b**	**3f**	82
13		**1a**	**3g**	74
14		**1b**	**3g**	63
15		**1a**	**3h**	67
16		**1b**	**3h**	24
17		**1a**	**3i**	66
18		**1b**	**3i**	nd
19		**1a**	**3j**	74
20		**1b**	**3j**	nd
21		**1a**	**3k**	73
22		**1b**	**3k**	46

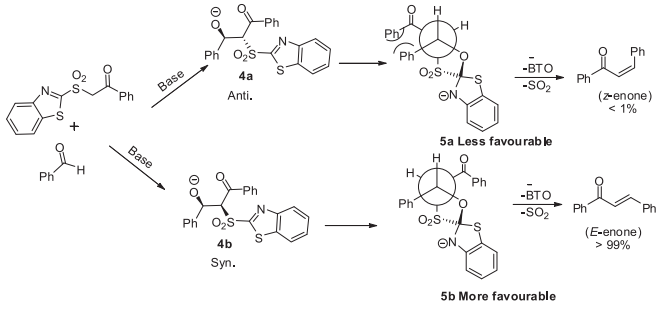
Table 2 (*continued*)

Entry	R^1	Act-	Product[c,d]	Yield[b]
23		**1a**	**3l**	78
24		**1b**	**3l**	64
25		**2a**	**3m**	69
26		**2b**	**3m**	43
27		**2a**	**3n**	76
28		**2b**	**3n**	64
29		**2a**	**3o**	79
30		**2b**	**3o**	69
31		**2a**	**3p**	81
32		**2b**	**3p**	80

[a] Reaction conditions: BT-sulfone (1.8 equiv), benzaldehyde (1 equiv), DBU (1.5 equiv), and time for the completion of reaction varies from 13 to 21 h.
[b] Isolated yield.
[c] All compounds characterized by mass, IR, ^{1}H NMR, ^{13}C NMR.
[d] *Z*/*E* ratio for all the products was >1:99% and determined by ^{1}H NMR/HPLC analysis.



Scheme 3. Plausible mechanism for the synthesis of enones.

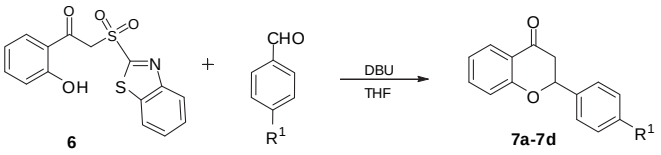


Scheme 4. Possible intermediates of the modified Julia olefination.

intermediate **5a** is less favorable. On the other hand the reaction proceeds via more stable intermediate **5b** resulting to the formation of *E*-conjugated enones in >99% stereoselectivity.

The versatility of developed Julia activators was utilized for the synthesis of flavanones via one-pot coupling reaction. 2-(Benzo[*d*]

thiazol-2-ylsulfonyl)-1-(2-hydroxyphenyl)ethanone (**6**) was reacted with benzaldehyde in the presence of DBU to furnish flavanones in moderate yield at refluxing condition, although corresponding chalcone was also formed as a side product (Scheme 5, Table 3).



Scheme 5. One-pot synthesis of flavanone.

Table 3
One-pot synthesis of flavanones based on Julia–Kocienski olefination[a]

Entry[c]	R^1	Product	Time (h)	Yield[b] (%)
1	H	**7a**	13	62
2	OCH_3	**7b**	11	68
3	OH	**7c**	18	40
4	Br	**7d**	16	65

[a] Reaction conditions: BT-sulfone (1.8 equiv), benzaldehyde (1 equiv), DBU (1.5 equiv), and time for the completion of reaction varies from 11–18 h at refluxing condition.
[b] Isolated yield.
[c] All compounds characterized by ^{1}H NMR.

In continuation to our antidiabetic drug discovery program,[35] some of newly developed Julia reagents were exhibiting promising anti-hyperglycemic activity and detail studies are in progress.

3. Conclusion

In summary, for the first time, we have demonstrated an application of Julia–Kocienski olefination reaction leading to the synthesis of chalcones and flavanones in high yields. We have also successfully developed new Julia coupling reagents for direct Julia–Kocienski olefination.

4. Experimental

4.1. Materials and general

All the reactions were carried out at room temperature, that is, 28–32 °C. Unless otherwise specified, all the reagents were purchased from Sigma–Aldrich Chemical Co., Lancaster and were used directly without further any purification. NMR spectra were obtained using the Brucker DRX 200 and 300 MHz spectrometers. Chemical shifts (δ) are given in parts per million relative to TMS, coupling constants (J) in hertz. IR spectra were taken on VARIAN FT-IR spectrometer as KBr pellets (when solid). Elemental analysis was preformed using a Perkin Elmer Autosystem XL Analyzer. Melting points were measured using a COMPLAB melting-point apparatus. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm silica gel plates visualized with UV light.

4.2. General procedure

*4.2.1. 2-(Benzo[d]thiazol-2-ylsulfonyl)-1-phenylethanone (**1a**)[33].* Benzo[*d*]thiazol-2-yl benzothioate (1 mmol) in 15 mL DCM was taken in 100 mL round bottom flask and *m*-CPBA (2.5 equiv) in DCM (25 mL) was taken into dropping funnel and added drop wise into solution of benzo[*d*]thiazol-2-yl benzothioate in THF. Reaction mixture was diluted with sodium bicarbonate solution and extracted by ethyl acetate. Ethyl acetate layer was dried, and evaporated under vacuum to give title compound as light yellow solid, R_f=0.33 (EtOAc/hexane 1:4, v/v), which was further recrystallized by methanol in 96% yield.

*4.2.1.1. (Benzo[d]thiazol-2-ylsulfonyl)(phenyl)methanone (**1a**)[33].* Physical state: solid, R_f=0.33 (EtOAc/hexane 1:4, v/v). Found: C, 56.73, H, 3.76, N, 4.53. $C_{15}H_{11}NO_3S_2$ requires C, 56.76; H, 3.49; N, 4.41%; IR (KBr) 2942, 1722, 1698, 1363 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) 5.1 (2H, s, CH_2CO), 7.37–7.58 (5H, m), 7.85–7.95 (3H, m), 8.09 (1H, d, J 7.41 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) 61.68, 123.64, 125.22, 128.25, 128.56, 129.17, 129.38, 134.82, 135.71, 136.83, 152.32, 188.75; MS (ES): m/z (%)=318.1(100) $[M+1]^+$.

*4.2.1.2. 2-(Benzo[d]thiazol-2-ylsulfonyl)-1-(4-methoxyphenyl) ethanone (**2a**)[33].* Physical state: solid, R_f=0.15 (EtOAc/hexane 1:4, v/v). Found: C, 55.26; H, 3.62; N, 3.92. $C_{16}H_{13}NO_4S_2$ requires C, 55.32; H, 3.77; N, 4.03%; IR (KBr) 2941, 1719, 1534, 1326 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) 3.91 (3H, s, OCH_3), 5.26 (2H, s, CH_2CO), 7.11 (2H, d, J 8.73 Hz), 7.31–7.42 (2H, m), 7.78 (2H, d, J 7.91 Hz), 8.03 (1H, d, J 7.77 Hz), 8.09 (2H, d, J 8.73 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) 55.48, 61.67, 121.39, 124.16, 128.22, 128.56, 129.02, 129.38, 134.77, 135.71, 136.81, 153.78, 184.73; MS (ES): m/z (%)=348 (100) $[M+1]^+$.

*4.2.1.3. 1-Phenyl-2-(1-phenyl-1H-tetrazole-5-sulfonyl)-ethanone (**1b**).* Physical state: yellow solid, R_f=0.25 (EtOAc/hexane 3:7, v/v). Found: C, 54.86; H, 3.62; N, 16.86. $C_{15}H_{12}N_4O_3S$ requires C, 54.87; H, 3.68; N, 17.06%; IR (KBr) 3104, 3041, 2975, 1721, 1363, 879 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) 5.25 (2H, s), 7.43–7.47 (2H, m), 7.51–7.65 (6H, m), 7.81–7.82 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) 62.48, 125.92, 128.94, 129.47, 129.85, 130.48, 131.81, 134.11, 135.34, 153.82, 187.26; MS (ES): m/z (%)=329 (100) $[M+1]^+$.

*4.2.1.4. 1-(4-Methoxyphenyl)-2-(1-phenyl-1H-tetrazol-5-ylsulfonyl)ethanone (**2b**).* Physical state: yellow solid, R_f=0.17 (EtOAc/hexane 3:7, v/v). Found: C, 53.62; H, 3.94; N, 15.63. $C_{16}H_{14}N_4O_4S$ requires C 53.59; H, 3.92; N, 16.87%; IR (KBr) 3098, 3041, 2972, 1711, 1365 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) 3.84 (3H, s), 5.25 (2H s), 7.21–7.25 (2H, m), 7.50–7.65(6H, m), 7.87–7.89(2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) 55.47, 62.43, 123.41, 128.26, 129.44, 129.38, 130.41, 131.54, 133.76, 138.54, 156.67, 186.83; MS (ES): m/z (%)=359 (100) $[M+1]^+$.

*4.2.1.5. 1-Phenyl-2-(pyridin-2-ylsulfonyl)ethanone (**1c**).* Physical state: light yellow solid, R_f=0.22 (EtOAc/hexane 1.5:4, v/v). Found: C, 59.73; H, 3.96; N, 5.13. $C_{13}H_{11}NO_3S$ requires C, 59.76; H, 4.24; N, 5.36%; IR (KBr) 1722, 1698, 1542, 1354, 789 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) 5.32 (2H, s, CH_2CO), 7.49–7.74 (5H, m), 7.92–8.37 (5H, m); ^{13}C NMR (75 MHz, $CDCl_3$) 64.37, 122.65, 127.24, 128.45, 128.89, 133.56, 136.72, 136.83, 154.37, 158.63, 188.75; MS (ES): m/z (%)=362 (100) $[M+1]^+$.

*4.2.1.6. 2-(3,5-Bis(trifluoromethyl)phenylsulfonyl)-1-phenyl-ethanone (**1d**).* Physical state: white solid, R_f=0.30 (EtOAc/hexane 3:7, v/v). Found: C, 48.38, H, 2.45. $C_{16}H_{10}F_6O_3S$ requires C, 48.49; H, 2.54%; IR (KBr) 2984, 2936, 1667, 1354, 1287, 821 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) 5.28 (2H, s, CH_2CO), 7.49 (2H, d, J 8.55 Hz), 7.82 (1H, m), 7.91(2H, d, J 8.55 Hz), 8.18 (1H, s), 8.41 (2H, s); ^{13}C NMR (75 MHz, $CDCl_3$) 63.33, 122.65 (q, J 274.5 Hz, $2CF_3$), 127.4, 128.25, 129.76, 129.38, 133.0 (q, J_{C-F}=35.2 Hz, $2CCF_3$), 133.56, 136.72, 136.83, 140.3, 187.05; MS (ES): m/z (%)=397 (100) $[M+1]^+$.

*4.2.2. Synthesis of 1,3-diphenyl-2-propen-1-one (**3a**) by Julia–Kocienski olefination reaction.* (Benzo[*d*]thiazol-2-ylsulfonyl)(phenyl)methanone 1 mmol (1.8 equiv) was taken in 50 mL round bottom flask in 10 mL THF, then DBU (1.5 equiv) was added and reaction mixture

was stirred about half an hour. Benzaldehyde (1 mmol) was added to the reaction mixture and further stirred the solution for about 16 h. THF was evaporated under reduced pressure and extracted by ethyl acetate. Ethyl acetate layer was dried, and evaporated under vacuum to give light yellow solid, R_f=0.54 (EtOAc/hexane 15:85, v/v), which was further recrystallized by ethanol. Organic layer was washed with water, brine (20 mL) solution, and evaporated under vacuum to give desired crude product, which, further purified by column chromatography. Yield (81%).

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2010.09.089.

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