Tetrahedron 68 (2012) 5053–5059

Contents lists available at SciVerse ScienceDirect

Tetrahedron

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

Study on comparison of reducing ability of three organic hydride compounds

Yi-Si Feng [a], Chun-Yan Yang [a], Qiang Huang [b], Hua-Jian Xu [b,*]

[a] School of Chemical Engineering, Hefei University of Technology, Hefei 230009, PR China
[b] School of Medical Engineering, Hefei University of Technology, Tunxi Road 193, Hefei 230009, PR China

ARTICLE INFO

Article history:
Received 13 January 2012
Received in revised form 9 April 2012
Accepted 12 April 2012
Available online 21 April 2012

Keywords:
Organic hydride compounds
Reducing ability
Irradiation

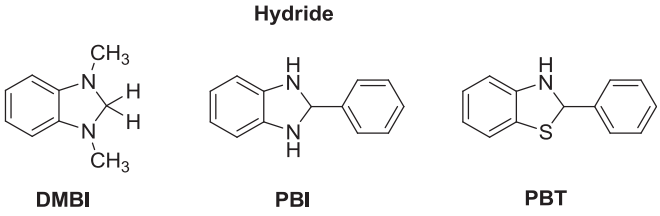
ABSTRACT

Selective reduction of three kinds of substrates were studied to evaluate the reducing abilities of *N*,*N*-dimethyl-benzimidazolidine (DMBI), 2-phenylbenzimidazoline (PBI) and 2-phenylbenzothiazoline (PBT). As hydride donors, these three five-membered heterocyclic compounds performed different reducing abilities depending on the substrates.

1. Introduction

Organic hydride compounds are one kind of substances, which can transfer hydrogen to the surrounding substrates in the form of hydride anions in chemical and biochemical reactions.[1] As we all know, there are many natural organic hydride donors in different forms in nature, such as NAD(P)H,[2] $FADH_2$,[3] Vitamin C[4] and tetrahydrofolate.[5] Many biomimetic hydrogen sources were synthesized by chemists in which the most widely studied were three six-membered heterocyclic compounds Hantzsch ester (HEH), 1-benzyl-1,4-dihydronicotinamide (BNAH) and 9,10-dihydroacridine ($AcrH_2$) with 1,4-dihydropyridine as active centre. They have been extensively studied by chemical workers as reducing agents, such as MacMillan,[6] List,[7] Rueping[8] and You.[9] At the same time, many five-membered heterocyclic compounds have been synthesized to transfer hydrogen to α,β-unsaturated compounds,[10] imines[11] and α,β-epoxy ketones.[12] Although these five-membered hydride compounds don't have 1,4-dihydropyridine structure, the proximity of hydride dissociation energy to NADH and high efficient hydride donating abilities they have also generated great interest of many chemists. However, although the theoretical data about five-membered heterocyclic hydride compounds have been reported,[13] such as the thermodynamic data of capacity of providing hydride anions, experimental studies on the comparison of their reducing abilities are lacking.

Herein, we chose three different five-membered heterocyclic hydride compounds, *N*,*N*-dimethylbenzimidazoline (DMBI), 2-phenylbenzimidazoline (PBI) and 2-phenylbenzothiazoline (PBT), to compare their abilities in reducing three kinds of substrates, α,β-epoxy ketones, electron-deficient olefins and α,β-unsaturated ketones. On the basis of exploring their reaction scope and properties, we committed to find the relationship between structure and activity. It will provide some protocols for designing the organic hydride compounds with more efficiently reducing abilities in future.



2. Results and discussion

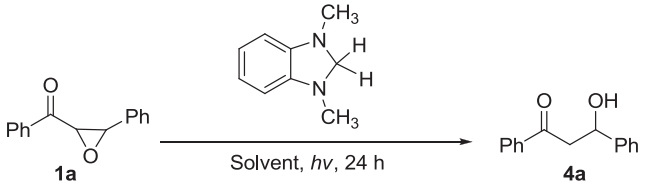
2.1. Reduction of α,β-epoxy ketones

Chemoselective reduction of α,β-epoxy ketones have attracted much attention for several decades because the reduction product (β-hydroxy ketones) were very important intermediates in organic synthesis.[12,14] Thus, in initial experiments we chose α,β-epoxy ketones as the reactive substrate to investigate the different catalytic efficiency of three hydride donors. At first, DMBI was used as hydride anion donor and the reaction parameters, such as solvent, time and loadings of DMBI were summarized in Table 1. In the

* Corresponding author. Tel.: +86 551 2904353; fax: +86 551 2904405; e-mail address: hjxu@hfut.edu.cn (H.-J. Xu).

0040-4020/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2012.04.047

Table 1
Hydrogenation of epoxy ketone **1a** with DMBI



Entry	Loadings (equiv)	Time (h)	Solvent	Yield[a] (%)
1	1.5	24	CH_3OH	—
2	1.5	24	THF	75
3	1.5	24	CH_3CN	68
4	1.5	24	Toluene	70
5	1.0	24	THF	30
6	2.0	24	THF	89
7	2.5	24	THF	87
8	2.0	12	THF	56
9	2.0	36	THF	88
10[b]	2.0	24	THF	—
11[c]	2.0	24	THF	90

[a] Isolated yield.
[b] 50 °C, without *hv*.
[c] With 10 mol % $AlCl_3$.

selective reduction of α,β-epoxy ketone **1a** to β-hydroxy ketones **4a**, the optimum reaction condition was irradiating at room temperature in THF (Table 1, entry 6). As shown, addition of Lewis acid could not significantly promote the yield. It was noteworthy that no product was obtained using proton solvent ethanol or without irradiation.

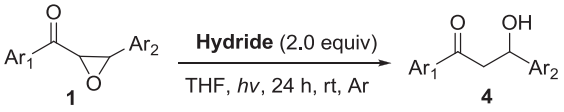
2-Phenylbenzimidazoline (PBI) is unstable in the air and easily oxidized to 2-pheny-benzimidazole according to the previous report.[10a] Therefore, in situ generation of PBI with *o*-phenylenediamine and benzaldehyde as raw materials, was used to reduce α,β-epoxy ketone. The optimum conditions about reduction of **1a** to β-hydroxy ketones **4a** were obtained by using PBI in 2.0 equiv under irradiation at room temperature for 24 h in THF (Table 2, entry 1).

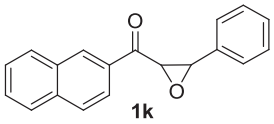
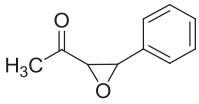
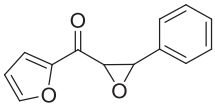
2-phenylbenzothiazoline (PBT), as a reducing agent, was used to transform hydrogen to **1a** to form β-hydroxy ketone **4a**. Among the selection of solvents, THF was also the best solvent and proton solvent ethanol was ineffective. Employing 2.0 equiv PBT under irradiation for 36 h was sufficient to complete the reaction in 91% yield (Table 2, entry 1).

Through the above studies we concluded that the reduction of α,β-epoxy ketones by organic hydride compounds didn't need Lewis acid as catalyst. Reactions accomplished sufficiently under irradiation at room temperature. Nevertheless, corresponding β-hydroxy ketone couldn't be obtained without irradiation because a possible mechanism was a photoinduced electron transfer process, which to be a useful way to generate ketyl radicals.[15] High-pressure mercury lamp can provide UV irradiation (λ>300 nm) to promote the hydride compounds to be excited and became radical cations. At the same time substrates converted to the corresponding radical anions via photoinduced electron transfer.[16] In the choice of solvent, employing a nonpolar solvent, such as THF could achieve good yields. However, proton solvent ethanol was inefficient. The potential reason was that the reaction process required two electrons and two protons, thereby protonic solvents would trap the radical and prevent the electron transfer and resulted in no target product.[12a]

As shown in Table 2, a series of α,β-epoxy ketones were reduced to the corresponding β-hydroxy ketones by DMBI, PBI and PBT, respectively, in the uniform conditions. In contrast to DMBI and PBT, the reduction of α,β-epoxy ketones by PBI generated in situ obtained more satisfactory results because of the comparatively stable yields (70–92%).

Table 2
Reduction of α,β-epoxy ketones by DMBI, PBI and PBT



Entry	Substrate	Product	Yield (%)		
			1[a]	2[b]	3[c]
1	**1a**: Ar_1=Ph, Ar_2=Ph	**4a**	89	88	87 (91)[d]
2	**1b**: Ar_1=*p*-F–C_6H_4, Ar_2=Ph	**4b**	37	70	40
3	**1c**: Ar_1=*p*-Cl–C_6H_4, Ar_2=Ph	**4c**	92	89	65
4	**1d**: Ar_1=*p*-Br, Ar_2=Ph	**4d**	88	92	52
5	**1e**: Ar_1=*p*-OCH_3–C_6H_4, Ar_2=Ph	**4e**	62	81	42
6	**1f**: Ar_1=*p*-CH_3–C_6H_4, Ar_2=Ph	**4f**	69	76	58
7	**1g**: Ar_1=Ph, Ar_2=*p*-Cl–C_6H_4	**4g**	87	87	83
8	**1h**: Ar_1=Ph, Ar_2=*o*-Cl–C_6H_4	**4h**	41	77	45
9	**1i**: Ar_1=Ph, Ar_2=*p*-Br–C_6H_4	**4i**	78	91	96
10	**1j**: Ar_1=Ph, Ar_2=*p*-OCH_3–C_6H_4	**4j**	42	79	76
11	 **1k**	**4k**	47	80	57
12	 **1l**	**4l**	33	83	49
13	 **1m**	**4m**	45	85	43

[a] Isolated yield. The reaction was reduced by DMBI.
[b] Isolated yield. The reaction condition was reduced by PBI.
[c] Isolated yield. The reaction condition was: PBT (2 equiv), THF (5 mL), *hv*, rt, 24 h.
[d] Isolated yield. The reaction was carried out in THF at ambient temperature for 36 h.

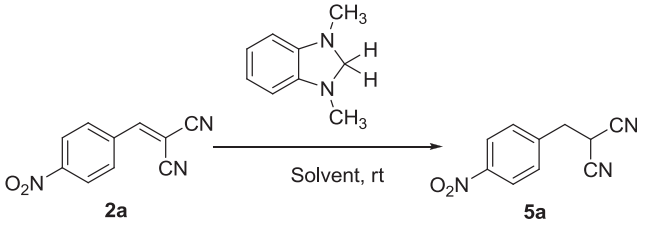
2.2. Reduction of electron-deficient olefins

From above, relatively satisfactory results were observed on the reducing abilities of three kinds of hydride donors by selective reduction of α,β-epoxy ketones. Then reduction of electron-deficient olefins carried with electron-withdrawing substituents by the three organic hydride compounds were investigated in this part. For optimizing the conditions, reduction of 2-(4-nitrobenzylidene) malononitrile **2a** by DMBI was chosen as model reaction. As shown, 93% yield was obtained by employing 1.5 equiv of DMBI in THF for 24 h (Table 3, entry 13). It was noteworthy that the amount of solvent became an important factor that using 7 mL solvent was better than 5 mL. However, the yields dropped unexpectedly as the solvent continuing to increase (Table 3, entries 11, 13–15).

Accordingly, a series of selection were carried out in order to find the appropriate conditions in reduction of electron-deficient olefin **2a** by PBI and PBT. The results showed that **2a** was reduced in the yield of 78% by PBI at room temperature in ethanol and was reduced by PBT in the yield of 81% at 80 °C in ethanol (Table 4, entry 1).

After optimized the reaction conditions, a range of cyano-substituted alkenes **2a**–**k** were reduced by DMBI, PBI and PBT in the same conditions. As presented in Table 4, when using DMBI as reductant, the substrates with phenyl, which was activated by strong electron-withdrawing group, such as nitro gave the corresponding reductive products in good yields (Table 4, entries 1–3). However, the substrates with halogen-substituted benzene **2h** and

Table 3
Optimization of reaction conditions for reduction of **2a** by DMBI



2a **5a**

Entry	Loadings (equiv)	Solvent (mL)	Time (h)	Yield[a] (%)
1	0.5	MeCN (5)	12	67
2	1.0	MeCN (5)	12	73
3	1.5	MeCN (5)	12	81
4	2.0	MeCN (5)	12	83
5	2.5	MeCN (5)	12	81
6[b]	1.5	MeCN (5)	12	82
7[c]	1.5	MeCN (5)	12	74
8	1.5	MeCN (5)	24	87
9	1.5	MeCN (5)	36	86
10	1.5	EtOH (5)	24	79
11	1.5	THF (5)	24	91
12	1.5	Benzene (5)	24	85
13	1.5	THF (7)	24	93
14	1.5	THF (9)	24	89
15	1.5	THF (11)	24	81

[a] Isolated yield.
[b] React with *hv*.
[c] React at 50 °C.

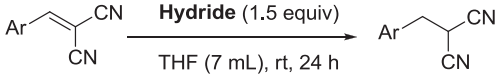
2i or alkenes jointed with furan **2e** or two phenyls **2j** or methyl and phenyl **2k** could hardly be reduced to the target products. As shown, olefins were reduced by PBI in comparatively good yields in THF or ethanol. However, reduction of electron-deficient olefins by PBT in this condition couldn't afford satisfactory results. Heating to 80 °C could effectively improve the yields. Apparently, we can conclude that reduction of electron-deficient olefins by DMBI and PBI proceed more easily than by PBT. Heating was an effective method to ensure high yields in reduction of olefins by PBT.

2.3. Reduction of α,β-unsaturated ketones

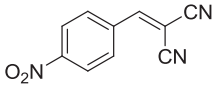
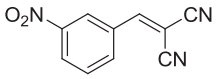
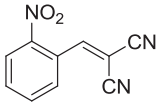
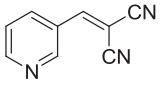
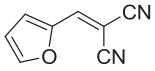
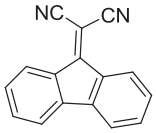
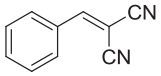
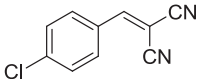
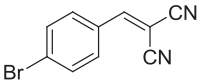
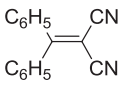
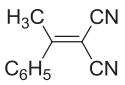
Selective hydrogenation of carbon–carbon double bond of α,β-unsaturated carbonyl compounds is a very important process in organic synthesis.[17] Therefore, reduction of α,β-unsaturated ketones to the corresponding saturated ketones by three hydride donors was studied. Compound **3i** was chosen as reaction substrate to find the optimized conditions. As shown in Table 5, a series of reaction parameters, such as the amount of DMBI, solvent, temperature, reaction time and Lewis acid were investigated. Among the catalyst tested, anhydrous magnesium perchlorate gave the best results (entries 3, 5–7). The optimal reaction conditions were utilizing 1.5 equiv of DMBI in toluene at 80 °C for 24 h (Table 5, entry 8). In our further study, only 48% **6i** was obtained with PBI as a reductant and zinc chloride as a catalyst (Table 6, entry 9). In contrast, **3i** was reduced in the yield of 75% by PBT with aluminium chloride as catalyst (Table 6, entry 9). In this process, Lewis acid played an important role and the possible course was that the metal ions of Lewis acid and the carbonyl oxygen of the substrates generated to a complex, which induced polarization of the carbon–carbon double bond.[10c]

As presented in Table 6, a series of α,β-unsaturated ketones were reduced to corresponding saturated ketones by three hydride donors in the same conditions. When using DMBI as reductant, the yields were 70–87% except **6k**. The substrates with phenyl carrying substituent and those of carbonyl group connected with

Table 4
Reduction of electron-deficient olefins by DMBI



2 **5**

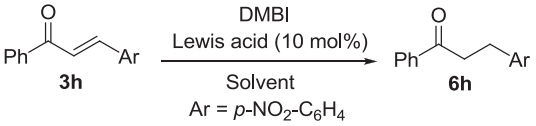
Entry	Substrate	Product		Yield (%)		
				1[a]	2[b]	3[c]
1		**2a**	**5a**	93	86 (88)[d]	— (81)[e]
2		**2b**	**5b**	87	84	—
3		**2c**	**5c**	84	80	—
4		**2d**	**5d**	85	89	—
5		**2e**	**5e**	—	26	—
6		**2f**	**5f**	78	75	—
7		**2g**	**5g**	86	83 (85)[d]	21 (91)[e]
8		**2h**	**5h**	—	52	—
9		**2i**	**5i**	—	95	—
10		**2j**	**5j**	—	—	—
11		**2k**	**5k**	—	—	—

[a] Isolated yield. The reaction was reduced by DMBI.
[b] Isolated yield. The reaction was reduced by PBI.
[c] Isolated yield. The reaction was reduced by PBT.
[d] The solvent was C_2H_5OH.
[e] Heat at 80 °C in C_2H_5OH.

heterocycle could give satisfactory yields. However, if the phenyl connected to carbonyl group was replaced by methyl, the ketone **3k** couldn't be reduced to the corresponding product **6k** (entry 11). In contrast, no products were obtained by using PBI and PBT as reducing donors in this reaction conditions. In order to prove the above reactions were not suitable for this system, reduction of **3a** and **3d** in their optimal conditions were studied. As a result, the reduction yields by using PBT as hydride donors were better than using PBI.

For testifying the method of optimization conditions was objective, we made a kinetic analysis. α,β-epoxy ketone **1a** was

Table 5
Optimization of reaction conditions for reduction of **3h** by DMBI



Entry	Loadings (equiv)	Solvent (mL)	Time (h)	Temp (°C)	Lewis acid	Yield (%)
1	1.5	Benzene	12	25	$Mg(ClO_4)_2$	—
2	1.5	Benzene	12	50	$Mg(ClO_4)_2$	48
3	1.5	Toluene	12	80	$Mg(ClO_4)_2$	73
4	1.5	Toluene	12	100	$Mg(ClO_4)_2$	74
5	1.5	Toluene	12	80	$FeCl_3$	64
6	1.5	Toluene	12	80	$AlCl_3$	61
7	1.5	Toluene	12	80	$ZnCl_2$	63
8	1.5	Toluene	24	80	$Mg(ClO_4)_2$	86
9	1.5	Toluene	36	80	$Mg(ClO_4)_2$	86
10	1.0	Toluene	24	80	$Mg(ClO_4)_2$	69
11	2.0	Toluene	24	80	$Mg(ClO_4)_2$	87
12	1.5	Toluene	24	80	—	—
13[a]	1.5	Toluene	24	80	$Mg(ClO_4)_2$	62
14[b]	1.5	Toluene	24	80	$Mg(ClO_4)_2$	87
15[c]	1.5	Toluene	24	80	$Mg(ClO_4)_2$	43

[a] $Mg(ClO_4)_2$ (5 mol %).
[b] $Mg(ClO_4)_2$ (20 mol %).
[c] Under air.

reduced by using PBT as reductant to find the reactivity under irradiation. We sampled the reaction solution quantitatively every 3 h during 48 h. Each sample was detected by HPLC and the results were presented in Fig. 1. To begin with, the yield of **4a** was increasing to 94% until 36 h as time went by. In contrast, the yield of **4a** was decreased when reaction duration was lengthened to 48 h. The possible cause was the happening of side reaction during long-period irradiation.

3. Conclusion

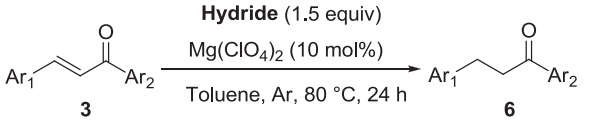
In summary, we studied the reduction of α,β-epoxy ketones, electron-deficient olefins and α,β-unsaturated ketones by three organic hydride compounds DMBI, PBI and PBT. Differences in reducing abilities of these hydride compounds were observed depending on the substrates. Base on the yields of product, we would like to conclude that reduction of α,β-epoxy ketones by PBI was more effective than the other two, but in the hydrogenation of electron-deficient olefins, DMBI and PBI achieved higher yields than PBT. In the selective reduction of α,β-unsaturated ketones, DMBI gained better results than the other two. Accordingly, all of these studies will make for the design of some new five-membered heterocyclic hydride compounds and would be a foundation for other people's research.

4. Experimental

4.1. General remarks

All the reduction reactions were carried out in oven-dried flasks of Schlenk tubes and conducted under a positive pressure of argon. DMBI[13b] and PBT[10c] were prepared by previously reported methods. In situ generation of PBI was processed directly by *o*-phenylenediamine and benzaldehyde.[10a] The α,β-epoxy ketones **1** were prepared from corresponding unsaturated ketones using alkaline hydrogen peroxide.[18] The olefins **2** were prepared by corresponding aldehydes and malononitrile with basic alumina.[19] The α,β-unsaturated ketones were prepared by corresponding acetophenone (**3a**–**j**) or acetone (**3k**) or heterocyclic ketones (**3l**, **3m**)

Table 6
Reduction of α,β-unsaturated ketones by DMBI



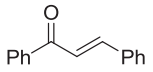
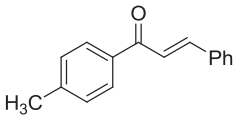
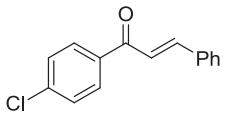
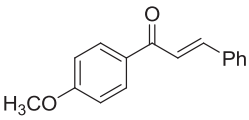
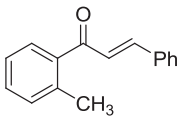
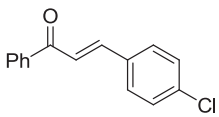
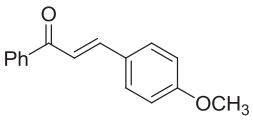
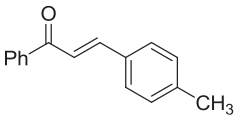
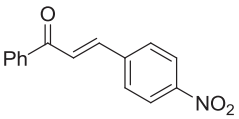
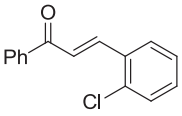
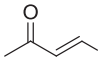
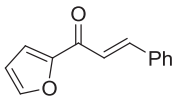
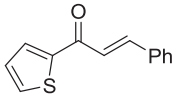
Entry	Substrate	Product		Yield (%)		
				1[a]	2[b]	3[c]
1		**3a**	**6a**	78	— (45)[d]	— (69)[e]
2		**3b**	**6b**	75	—	—
3		**3c**	**6c**	79	—	—
4		**3d**	**6d**	75	— (42)[d]	— (65)[e]
5		**3e**	**6e**	70	—	—
6		**3f**	**6f**	82	—	—
7		**3g**	**6g**	79	—	—
8		**3h**	**6h**	76	—	
9		**3i**	**6i**	86	— (48)[d]	— (75)[e]
10		**3j**	**6j**	80	—	—
11		**3k**	**6k**	—	—	—

Table 6 (*continued*)

Entry	Substrate	Product		Yield (%)		
				1[a]	2[b]	3[c]
12		**3l**	**6l**	87	—	—
13		**3m**	**6m**	86	—	—

[a] Isolated yield. The reaction was reduced by DMBI.
[b] Isolated yield. The reaction was reduced by PBI.
[c] Isolated yield. The reaction was reduced by PBT.
[d] Reaction was carried out in the presence of 40 mol % $ZnCl_2$ in C_2H_5OH.
[e] Reaction was carried out in the presence of 40 mol % $AlCl_3$ in C_2H_5OH.

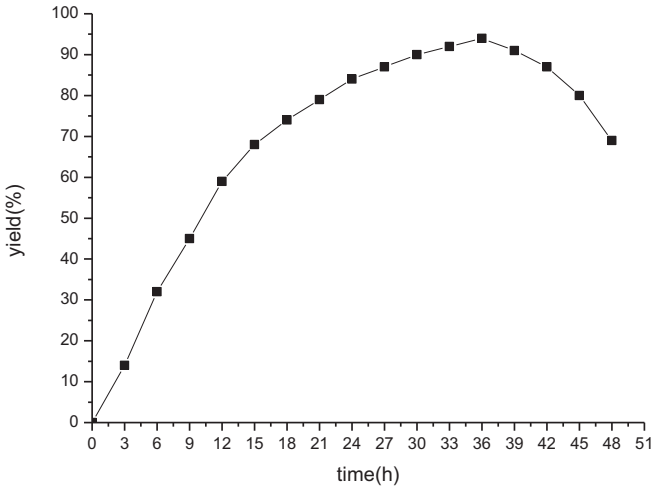


Fig. 1. Relations between yield and time in reduction of **1a** by PBT.

and benzaldehyde with NaOH at room temperature.[20] Other reagents and solvents were purchased and used without further purification. Analytical thin layer chromatography (TLC) was performed using Merck silica gel GF_{254} plates. Flash column chromatography was performed with silica gel (200–300 mesh). Gas chromatographic (GC) analysis was performed on a Shimadzu GC-2014 Series GC System. High performance liquid chromatography (HPLC) was performed on a Waters 2487 UV detector. The ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a 300 MHz instrument with TMS as internal standard.

4.1.1. N,N-Dimethylbenzimidazoline (DMBI).[13] ^1H NMR (300 MHz, $CDCl_3$) δ 6.62 (dd, J=3.3, 5.4 Hz, 2H), 6.35 (dd, J=3.3, 5.4 Hz, 2H), 4.27 (s, 2H), 2.67 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.15, 119.12, 112.66, 80.23, 33.61.

4.1.2. 2-Phenylbenzothiazoline (PBT).[10c] ^1H NMR (300 MHz, $CDCl_3$) δ 7.56–7.53 (m, 2H), 7.40–7.29 (m, 3H), 7.05 (d, J=7.5 Hz, 1H), 6.95 (t, J=7.6 Hz, 1H), 6.76 (t, J=7.2 Hz, 1H), 6.66 (d, J=7.7 Hz, 1H), 6.38 (s, 1H), 4.33 (br s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.26, 141.66, 129.02, 128.76, 128.72, 126.54, 125.48, 121.62, 120.65, 109.71, 69.98.

4.2. General procedure for reduction of α,β-epoxy ketones

A solution of a α,β-epoxy ketone substrate (0.5 mmol) and DMBI (0.5–1.25 mmol) or *o*-phenylenediamine (0.5 mmol) and benzaldehyde (0.5 mmol) or PBT (0.5–1.5 mmol) with or without Lewis acid in tetrahydrofuran (5 mL) or other solvents was irradiated with a 450 W high-pressure mercury lamp in a Schlenk tubes under an argon atmosphere at room temperature for 12–36 h. The irradiated reaction was monitored by TLC. After completion of the reaction, 1 mL HCl (0.1 mol/L) was added to the solution and stirred for 10 min, and then the solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel and the obtained corresponding β-hydroxy ketones were identified by ^1H and ^{13}C NMR.

*4.2.1. 3-Hydroxy-1,3-diphenylpropan-1-one (**4a**).*[21] ^1H NMR (300 MHz, $CDCl_3$) δ 7.96 (d, J=7.2 Hz, 2H), 7.59 (t, J=7.4 Hz, 1H), 7.53–7.22 (m, 7H), 5.35 (t, J=6.0 Hz, 1H), 3.61 (s, 1H), 3.38 (d, J=6.0 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.27, 144.93, 136.56, 133.73, 128.76, 128.63, 128.20, 127.74, 125.80, 70.06, 47.43.

*4.2.2. 1-(4-Fluorophenyl)-3-hydroxy-3-phenylpropan-1-one (**4b**).*[21] ^1H NMR (300 MHz, $CDCl_3$) δ 8.01–7.97 (m, 2H), 7.45–731 (m, 5H), 7.14 (t, J=8.6 Hz, 2H), 5.42–5.29 (m, 1H), 3.50 (s, 1H), 3.38–3.32 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.42, 167.78, 142.94, 130.94, 130.82, 128.62, 127.76, 125.75, 116.01, 115.71, 70.08, 47.38.

*4.2.3. 1-(4-Chlorophenyl)-3-hydroxy-3-phenylpropan-1-one (**4c**).*[21] ^1H NMR (300 MHz, $CDCl_3$) δ 7.88 (d, J=8.7 Hz, 2H), 7.45–7.25 (m, 7H), 5.36–5.32 (m, 1H), 3.49 (s, 1H), 3.33 (t, J=6.4 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.79, 142.88, 140.17, 134.98, 129.60, 129.06, 128.64, 127.80, 125.74, 70.03, 47.46.

*4.2.4. 1-(4-Bromophenyl)-3-hydroxy-3-phenylpropan-1-one (**4d**).*[21] ^1H NMR (300 MHz, $CDCl_3$) δ 7.82 (d, J=8.6 Hz, 2H), 7.61 (d, J=8.6 Hz, 2H), 7.49–7.27 (m, 5H), 5.37–5.33 (m, 1H), 3.76 (br s, 1H), 3.34 (t, J=8.4 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.04, 142.83, 135.32, 132.08, 130.08, 129.70, 128.67, 127.83, 125.76, 70.00, 47.46.

*4.2.5. 3-Hydroxy-1-(4-methoxyphenyl)-3-phenylpropan-1-one (**4e**).*[21] ^1H NMR (300 MHz, $CDCl_3$) δ 7.94 (d, J=9.0 Hz, 2H), 7.52–7.26 (m, 5H), 6.93 (d, J=9.0 Hz, 2H), 5.35–5.31 (m, 1H), 3.87 (s, 3H), 3.76 (br s, 1H), 3.33–3.30 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.31, 165.46, 144.56, 132.02, 131.14, 130.05, 129.12, 127.27, 115.36, 71.67, 57.03, 48.42.

*4.2.6. 3-Hydroxy-3-phenyl-1-p-tolylpropan-1-one (**4f**).*[21] ^1H NMR (300 MHz, $CDCl_3$) δ 7.94 (d, J=8.9 Hz, 2H), 7.49–7.28 (m, 5H), 6.93 (d, J=8.9 Hz, 2H), 5.35–5.31 (m, 1H), 3.90 (s, 1H), 3.87 (s, 3H), 3.33–3.30 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.84, 143.95, 143.09, 132.04, 130.54, 128.58, 127.65, 125.80, 113.89, 70.19, 55.56, 46.95.

*4.2.7. 3-(4-Chlorophenyl)-3-hydroxy-1-phenylpropan-1-one (**4g**).*[21] ^1H NMR (300 MHz, $CDCl_3$) δ 7.95 (d, J=7.2 Hz, 2H), 7.60 (t, J=7.4 Hz, 1H), 7.47 (t, J=7.4 Hz, 2H), 7.42–7.30 (m, 4H), 5.34–5.30 (m, 1H), 3.69 (s, 1H), 3.38–3.31 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.02, 141.46, 136.42, 133.85, 133.36, 128.80, 128.73, 128.18, 127.20, 69.43, 47.27.

*4.2.8. 3-(2-Chlorophenyl)-3-hydroxy-1-phenylpropan-1-one (**4h**).*[21] ^1H NMR (300 MHz, $CDCl_3$) δ 7.97 (d, J=7.2 Hz, 2H), 7.72 (d, J=7.8 Hz, 1H), 7.60 (t, J=7.2 Hz, 1H), 7.47 (t, J=7.8 Hz, 2H), 7.34 (t, J=7.2 Hz, 2H), 7.21–7.26 (m, 1H), 5.69 (d, J=9.6 Hz, 1H), 3.80 (br s, 1H), 3.60–3.10 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.37, 140.35, 136.43, 133.80, 131.19, 129.38, 128.77, 128.64, 128.25, 127.30, 66.85, 45.39.

*4.2.9. 3-(4-Bromophenyl)-3-hydroxy-1-phenylpropan-1-one (**4i**).*[22] ^1H NMR (300 MHz, $CDCl_3$) δ 7.95 (d, J=8.4 Hz, 2H), 7.60–7.45 (m, 5H), 7.32 (d, J=8.1 Hz, 2H), 5.33–5.29 (m, 1H), 3.65 (br s, 1H), 3.38–3.28

(m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.96, 142.03, 136.40, 133.85, 131.67, 128.80, 128.20, 127.57, 121.46, 69.46, 47.24.

*4.2.10. 3-Hydroxy-3-(4-methoxyphenyl)-1-phenylpropan-1-one (**4j**).*[21] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 (d, *J*=7.2 Hz, 2H), 7.59 (t, *J*=7.2 Hz, 1H), 7.46 (t, *J*=7.8 Hz, 2H), 7.37 (d, *J*=8.7 Hz, 2H), 6.91 (d, *J*=8.7 Hz, 2H), 5.36–5.23 (m, 1H), 3.81 (s, 3H), 3.56 (s, 1H), 3.40–3.31 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.30, 159.15, 136.62, 135.17, 133.67, 128.74, 128.20, 127.08, 113.96, 69.71, 55.34, 47.38.

*4.2.11. 3-Hydroxy-1-(naphthalen-2-yl)-3-phenylpropan-1-one (**4k**).*[21] ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.45 (s, 1H), 7.94–7.86 (m, 4H), 7.60–7.35 (m, 7H), 5.41 (t, *J*=6.0 Hz, 1H), 3.66 (br s, 1H), 3.51 (d, *J*=6.0 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.07, 144.78, 133.94, 132.45, 130.18, 129.62, 128.98, 128.60, 127.81, 127.71, 126.93, 126.79, 125.80, 123.56, 70.18, 47.50.

*4.2.12. 4-Hydroxy-4-phenylbutan-2-one (**4l**).*[21] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J*=4.4 Hz, 4H), 7.29–7.26 (m, 1H), 5.13 (dd, *J*=3.3, 9.0 Hz, 1H), 3.37 (br s, 1H), 2.91–2.76 (m, 2H), 2.17 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.12, 142.90, 128.62, 127.75, 125.72, 69.94, 52.08, 30.83.

*4.2.13. 1-(2-Furyl)-3-hydroxy-3-phenylpropan-1-one (**4m**).*[21] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 (s, 1H), 7.49–7.19 (m, 6H), 6.56–6.55 (m, 1H), 5.40–5.24 (t, *J*=6.0 Hz, 1H), 3.43 (s, 1H), 3.30–3.21 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 188.69, 147.02, 142.86, 128.60, 127.77, 125.76, 118.12, 112.53, 70.06, 47.03.

4.3. General procedure for reduction of electron-deficient olefins

A solution of the olefin (0.5 mmol) and DMBI (0.25–1.25 mmol) or *o*-phenylenediamine (0.5 mmol) and benzaldehyde (0.5 mmol) or PBT (0.5–1.5 mmol) in acetonitrile (5 mL) or other solvent (5–11 mL) at room temperature or other conditions was stirred in a Schlenk tubes for 12–36 h under an argon atmosphere. The reaction was monitored by GC. After completion of the reaction, appropriate amount of HCl (0.1 mol/L) was added to the solution and stirred for 10 min, and then the resulted solution was concentrated under reduced pressure and the residue followed by column chromatography on silica gel and the obtained corresponding malononitriles were identified by ^{1}H and ^{13}C NMR.

*4.3.1. 2-(4-Nitrobenzyl)malononitrile (**5a**).*[23] ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.26 (d, *J*=9.0 Hz, 2H), 7.51 (d, *J*=9.0 Hz, 2H), 4.04 (t, *J*=6.0 Hz, 1H), 3.41 (d, *J*=6.6 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.2, 145.1, 130.45, 124.54, 111.50, 36.09, 24.46.

*4.3.2. 2-(3-Nitrobenzyl)malononitrile (**5b**).*[23] ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.27 (t, *J*=9.0 Hz, 2H), 7.63–7.74 (m, 2H), 4.04 (t, *J*=6.8 Hz, 1H), 3.44 (d, *J*=9.0 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.47, 140.03, 135.43, 130.56, 124.27, 124.06, 111.52, 36.07, 24.61.

*4.3.3. 2-(2-Nitrobenzyl)malononitrile (**5c**).*[23] ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14 (d, *J*=7.1 Hz, 1H), 7.74–7.53 (m, 3H), 4.42 (t, *J*=7.8 Hz, 1H), 3.57 (d, *J*=7.8 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.69, 134.63, 133.97, 130.51, 128.35, 126.04, 112.10, 35.02, 23.68.

*4.3.4. 2-(Pyridin-3-ylmethyl)malononitrile (**5d**).*[23] ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.78–8.50 (m, 2H), 7.72 (d, *J*=7.8 Hz, 1H), 7.37 (t, *J*=9.0 Hz, 1H), 3.99 (t, *J*=6.6 Hz, 1H), 3.32 (d, *J*=6.6 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.36, 150.28, 143.01, 136.90, 124.03, 111.71, 33.95, 24.74.

*4.3.5. 2-(Furan-2-ylmethyl)malononitrile (**5e**).*[23] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 (s, 1H), 6.46–6.32 (m, 2H), 4.07 (t, *J*=7.2 Hz, 1H), 3.38 (d, *J*=7.2 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.57, 143.09, 114.45, 110.92, 109.98, 29.77, 22.66.

*4.3.6. 2-(9H-Fluoren-9-yl)malononitrile (**5f**).*[24] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82–7.75 (m, 4H), 7.51 (t, *J*=7.5 Hz, 2H), 7.41 (t, *J*=7.5 Hz, 2H), 4.40 (d, *J*=5.1 Hz, 1H), 4.24 (d, *J*=5.3 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.45, 139.66, 129.77, 128.15, 124.71, 120.83, 111.52, 46.02, 27.84.

*4.3.7. 2-Benzylmalononitrile (**5g**).*[10a] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.38 (m, 3H), 7.33–7.31 (m, 2H), 3.91 (t, *J*=6.9 Hz, 1H), 3.28 (d, *J*=6.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.27, 129.64, 129.46, 129.16, 112.49, 37.07, 25.31.

*4.3.8. 2-(4-Chlorobenzyl)malononitrile (**5h**).*[23] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J*=7.5 Hz, 2H), 7.23 (d, *J*=7.5 Hz, 2H), 3.90 (t, *J*=6.9 Hz, 1H), 3.25 (d, *J*=6.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.89, 130.96, 129.78, 128.88, 111.81, 35.39, 24.63.

*4.3.9. 2-(4-Bromobenzyl)malononitrile (**5i**).*[23] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J*=7.3 Hz, 2H), 7.38 (d, *J*=5.7 Hz, 2H), 3.96 (t, *J*=7.0 Hz, 1H), 3.34 (d, *J*=7.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.59, 131.95, 130.78, 123.48, 112.80, 36.35, 24.73.

4.4. General procedure for reduction of α,β-unsaturated ketones

A solution of the α,β-unsaturated ketone (0.5 mmol) and DMBI (0.5–1.0 mmol) or *o*-phenylenediamine (0.5 mmol) and benzaldehyde (0.5 mmol) or PBT (0.5–1.5 mmol) in benzene (7 mL) or toluene (7 mL) in the presence of a Lewis acid (5–20 mol %) was stirred in a Schlenk tubes at 25–80 °C for 12–48 h under an argon atmosphere. The reaction was monitored by TLC. After completion of the reaction, 1 mL HCl (0.1 mol/L) was added to the solution and stirred for 10 min, and then the resulted aqueous mixture was concentrated under reduced pressure and the residue followed by column chromatography on silica gel and the obtained corresponding saturated ketones were identified by ^{1}H and ^{13}C NMR.

*4.4.1. 1,3-Diphenylpropan-1-one (**6a**).*[10c] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 (d, *J*=9.6 Hz, 2H), 7.61–7.50 (m, 1H), 7.49–7.39 (m, 2H), 7.35–7.18 (m, 5H), 3.30 (t, *J*=7.2 Hz, 2H), 3.14–2.99 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.17, 140.28, 135.88, 132.01, 127.58, 127.50, 127.40, 127.02, 125.11, 39.41, 29.13.

*4.4.2. 3-Phenyl-1-p-tolylpropan-1-one (**6b**).*[25] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (d, *J*=8.1 Hz, 2H), 7.23–7.11 (m, 7H), 3.19 (t, *J*=7.8 Hz, 2H), 3.04–2.92 (m, 2H), 2.32 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.80, 142.75, 140.38, 133.41, 128.24, 127.47, 127.39, 127.13, 125.06, 39.28, 29.20, 20.57.

*4.4.3. 1-(4-Chlorophenyl)-3-phenylpropan-1-one (**6c**).*[25] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95–7.75 (m, 2H), 7.64–7.29 (m, 3H), 7.28–7.06 (m, 4H), 3.19 (t, *J*=7.8 Hz, 2H), 2.98 (t, *J*=7.5 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.98, 141.10, 139.52, 135.20, 130.79, 129.96, 129.49, 128.95, 128.61, 128.45, 126.26, 40.45, 30.08.

*4.4.4. 1-(4-Methoxyphenyl)-3-phenylpropan-1-one (**6d**).*[25] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (d, *J*=8.4 Hz, 2H), 7.37–7.12 (m, 5H), 6.92 (d, *J*=8.4 Hz, 2H), 3.86 (s, 3H), 3.32–3.19 (m, 2H), 3.13–2.98 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.86, 163.48, 141.51, 130.35, 129.97, 128.55, 128.48, 126.13, 113.76, 55.50, 40.17, 30.35.

*4.4.5. 3-Phenyl-1-o-tolylpropan-1-one (**6e**).*[26] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (d, *J*=7.5 Hz, 1H), 7.21–7.06 (m, 8H), 3.13 (t, *J*=7.2 Hz, 2H), 2.95 (t, *J*=7.8 Hz, 2H), 2.38 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$)

δ 202.29, 140.16, 137.02, 136.91, 130.91, 130.17, 127.46, 127.38, 127.31, 125.07, 124.61, 42.17, 29.30, 20.17.

*4.4.6. 3-(4-Chlorophenyl)-1-phenylpropan-1-one (**6f**).*[25] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 (d, *J*=7.2 Hz, 2H), 7.46 (t, *J*=7.2 Hz, 1H), 7.35 (t, *J*=7.5 Hz, 2H), 7.21–7.12 (m, 2H), 7.08 (d, *J*=8.4 Hz, 2H), 3.18 (t, *J*=7.5 Hz, 2H), 2.95 (t, *J*=7.5 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.73, 138.72, 135.75, 132.10, 130.83, 128.79, 127.59, 127.55, 126.96, 39.06, 28.34.

*4.4.7. 3-(4-Methoxyphenyl)-1-phenylpropan-1-one (**6g**).*[25] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 (d, *J*=7.2 Hz, 2H), 7.55 (t, *J*=7.2 Hz, 1H), 7.45 (t, *J*=7.5 Hz, 2H), 7.17 (d, *J*=8.4 Hz, 2H), 6.84 (d, *J*=8.7 Hz, 2H), 3.78 (s, 3H), 3.27 (t, *J*=7.5 Hz, 2H), 3.01 (t, *J*=7.5 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.41, 158.04, 136.94, 133.35, 133.07, 129.40, 128.64, 128.08, 113.98, 55.30, 40.73, 29.32.

*4.4.8. 1-Phenyl-3-p-tolylpropan-1-one (**6h**).*[27] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 (d, *J*=8.1 Hz, 2H), 7.36–7.12 (m, 8H), 3.27 (t, *J*=7.5 Hz, 2H), 3.11–3.00 (m, 2H), 2.40 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.22, 137.16, 135.89, 134.55, 131.95, 128.16, 127.54, 127.25, 126.99, 39.53, 28.69, 19.95.

*4.4.9. 3-(4-Nitrophenyl)-1-phenylpropan-1-one (**6i**).*[28] ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.16 (d, *J*=8.6 Hz, 2H), 7.96 (d, *J*=7.2 Hz, 2H), 7.72–7.35 (m, 5H), 3.37 (t, *J*=7.5 Hz, 2H), 3.19 (t, *J*=7.2 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.19, 149.27, 136.92, 136.51, 133.44, 129.41, 128.76, 128.02, 123.79, 39.42, 29.74.

*4.4.10. 3-(2-Chlorophenyl)-1-phenylpropan-1-one (**6j**).*[27] ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01–7.90 (m, 2H), 7.54 (t, *J*=7.2 Hz, 1H), 7.44 (t, *J*=7.5 Hz, 2H), 7.36–7.29 (m, 2H), 7.22–7.10 (m, 2H), 3.33–3.27 (m, 2H), 3.21–3.15 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.89, 137.82, 135.76, 132.91, 132.05, 129.76, 128.52, 127.56, 127.02, 126.69, 125.93, 37.40, 27.31.

*4.4.11. 1-(2-Furyl)-3-phenylpropan-1-one (**6l**).*[26] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 (d, *J*=0.9 Hz, 1H), 7.51–7.37 (m, 1H), 7.37–7.12 (m, 5H), 6.52–6.61 (m, 1H), 3.22–3.10 (m, 2H), 3.07–3.01 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 188.58, 152.63, 146.45, 140.99, 128.57, 128.46, 126.23, 117.20, 112.29, 40.19, 29.98.

*4.4.12. 3-Phenyl-1-(thiophen-2-yl)propan-1-one (**6m**).*[26] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (d, *J*=4.8 Hz, 1H), 7.53 (dd, *J*=0.9, 4.8 Hz, 1H), 7.27–7.07 (m, 5H), 7.04–7.01 (m, 1H), 3.20–3.10 (m, 2H), 3.04–2.93 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.06, 143.13, 139.95, 132.49, 130.77, 127.50, 127.38, 127.05, 125.16, 40.06, 29.34.

4.5. Kinetic measurement

A solution of a α,β-epoxy ketone substrate **1a** (1 mmol) and PBT (2 mmol) in tetrahydrofuran (10 mL) was irradiated with a 450 W high-pressure mercury lamp in a Schlenk tubes under an argon atmosphere at room temperature for 48 h. Every 3 h 0.5 mL reaction solution was took out under the protection of argon atmosphere. The yield of corresponding β-hydroxy ketone **4a** was monitored by HPLC.

Acknowledgements

We gratefully acknowledge financial support from the National Natural Science Foundation of China (Nos. 20802015, 21072040, 21071040) and the Program for New Century Excellent Talents in University of the Chinese Ministry of Education (NCET-11-0627).

Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2012.04.047. These data include MOL files and InChiKeys of the most important compounds described in this article.

References and notes

1. (a) Deno, N. C.; Peterson, J.; Saines, G. S. *Chem. Rev.* **1960**, *60*, 7 and references cited therein; (b) Ian, C.; Watt, F. *Adv. Phys. Org. Chem.* **1988**, *24*, 59 and references cited therein.
2. (a) Murakami, Y.; Kikuchi, J.-I.; Hisaeda, Y.; Hayashida, O. *Chem. Rev.* **1996**, *96*, 721; (b) Stout, D. M.; Meyers, A. I. *Chem. Rev.* **1982**, *82*, 223; (c) Eisner, U.; Kuthan, J. *Chem. Rev.* **1972**, *72*, 1.
3. (a) Bruice, T. C. *Acc. Chem. Res.* **1980**, *13*, 256; (b) Walsh, C. *Acc. Chem. Res.* **1980**, *13*, 148; (c) Walsh, C. *Acc. Chem. Res.* **1986**, *19*, 216; (d) Fitzpatrick, P. F. *Acc. Chem. Res.* **2001**, *34*, 299.
4. (a) Karrer, P. *Chem. Rev.* **1934**, *14*, 17; (b) Neta, P. *Chem. Rev.* **1972**, *72*, 533.
5. (a) Stroud, R. M.; Finer-Moore, J. S. *Biochemistry* **2003**, *42*, 239 and references cited therein; (b) Finer-Moore, J. S.; Santi, D. V.; Stroud, R. M. *Biochemistry* **2003**, *42*, 248 and references cited therein; (c) Hong, B. Y.; Haddad, M.; Maley, F.; Jensen, J. H.; Kohen, A. *J. Am. Chem. Soc.* **2006**, *128*, 5636.
6. (a) Ouellet, S. G.; Tuttle, J. B.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2005**, *127*, 32; (b) Storer, R. I.; Carrera, D. E.; Ni, Y.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2006**, *128*, 84; (c) Tuttle, J. B.; Ouellet, S. G.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2006**, *128*, 12662.
7. (a) Yang, J. W.; Hechavarria Fonseca, M. T.; List, B. *Angew. Chem., Int. Ed.* **2004**, *43*, 6660; (b) Yang, J. W.; Hechavarria Fonseca, M. T.; Vignola, N.; List, B. *Angew. Chem., Int. Ed.* **2005**, *44*, 108; (c) Hoffmann, S.; Seayad, A. M.; List, B. *Angew. Chem., Int. Ed.* **2005**, *44*, 7424; (d) Mayer, S.; List, B. *Angew. Chem., Int. Ed.* **2006**, *45*, 4193; (e) Hoffmann, S.; Nicoletti, M.; List, B. *J. Am. Chem. Soc.* **2006**, *128*, 13074; (f) Martin, N. J. A.; List, B. *J. Am. Chem. Soc.* **2006**, *128*, 13368; (g) Zhou, J.; List, B. *J. Am. Chem. Soc.* **2007**, *129*, 7498; (h) Martin, N. J. A.; Ozores, L.; List, B. *J. Am. Chem. Soc.* **2007**, *129*, 8976.
8. (a) Rueping, M.; Sugiono, E.; Azap, C.; Theissmann, T.; Bolte, M. *Org. Lett.* **2005**, *7*, 3781; (b) Rueping, M.; Antonchick, A. P.; Theissmann, T. *Angew. Chem., Int. Ed.* **2006**, *45*, 3683; (c) Rueping, M.; Antonchick, A. P.; Theissmann, T. *Angew. Chem., Int. Ed.* **2006**, *45*, 6751; (d) Rueping, M.; Antonchick, A. P. *Angew. Chem., Int. Ed.* **2007**, *46*, 4562.
9. (a) Kang, Q.; Zhao, Z. A.; You, S. L. *Adv. Synth. Catal.* **2007**, *349*, 1657; (b) You, S. L. *Chem.—Asian. J.* **2007**, *2*, 820.
10. (a) Chikashita, H.; Nishida, S.; Miyazaki, Y. M.; Itoh, K. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 737; (b) Chikashita, H.; Miyaazaki, M.; Itoh, K. *Synthesis* **1984**, 308; (c) Chikashita, H.; Miyazaki, M.; Itoh, K. *J. Chem. Soc., Perkin Trans. 1* **1987**, 699; (d) Chikashita, H.; Itoh, K. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 1747.
11. (a) Zhu, C.; Akiyama, T. *Org. Lett.* **2009**, *11*, 4180; (b) Zhu, C.; Akiyama, T. *Adv. Synth. Catal.* **2010**, *352*, 1846; (c) Henseler, A.; Kato, M.; Mori, K.; Akiyama, T. *Angew. Chem., Int. Ed.* **2011**, *50*, 8180.
12. (a) Hasegawa, E.; Kato, T.; Kitazume, T.; Yanagi, K.; Hasegawa, K.; Horaguchi, T. *Tetrahedron Lett.* **1996**, *37*, 7079; (b) Hasegawa, E.; Takizawa, S.; Seida, T.; Yamaguchi, A.; Yamaguchi, N.; Chiba, N.; Takahashi, T.; Ikeda, H.; Akiyama, K. *Tetrahedron* **2006**, *62*, 6581.
13. (a) Zhu, X. Q.; Yang, Y.; Zhang, M.; Cheng, J. P. *J. Am. Chem. Soc.* **2003**, *125*, 15298; (b) Zhu, X. Q.; Zhang, M. T.; Yu, A.; Wang, C. H.; Cheng, J. P. *J. Am. Chem. Soc.* **2008**, *130*, 2501.
14. (a) Robinson, C. H.; Henderson, R. *J. Org. Chem.* **1972**, *37*, 565; (b) Weile, G. R.; McMorris, T. C. *J. Org. Chem.* **1978**, *43*, 3942; (c) McChesney, J. D.; Thompson, T. N. *J. Org. Chem.* **1985**, *50*, 3473; (d) Inokuchi, T.; Kusumoto, M.; Torii, S. *J. Org. Chem.* **1990**, *55*, 1548; (e) Engman, L.; Stern, D. *J. Org. Chem.* **1994**, *59*, 5179.
15. (a) Fox M.A.; Chanon M., Eds. Elsevier, Amsterdam, 1988. (b) Yoon, U. C.; Mariano, P. S.; Givens, R. S.; Atwater III, B. W. *Adv. Electron Transfer Chem.* **1994**, *4*, 117 and references cited therein.
16. Zhang, J.; Jin, M. Z.; Zhang, W.; Yang, L.; Liu, Z. L. *Tetrahedron Lett.* **2002**, *43*, 9687.
17. Adolfsson, H. *Angew. Chem., Int. Ed.* **2005**, *44*, 3340.
18. Hasegawa, E.; Ishiyama, K.; Horaguchi, T.; Shimizu, T. *J. Org. Chem.* **1991**, *56*, 1631.
19. Texeir-Boullet, F.; Foucaud, A. *Tetrahedron Lett.* **1982**, *23*, 4927.
20. Toda, F.; Tanaka, K.; Hamai, K. *J. Chem. Soc., Perkin Trans. 1* **1990**, 3207.
21. Xu, H. J.; Liu, Y. C.; Fu, Y.; Wu, Y. D. *Org. Lett.* **2006**, *8*, 3449.
22. Wiles, C.; Watts, P.; Haswell, S. J.; Pombo-Villar, E. *Tetrahedron* **2005**, *61*, 10757.
23. Tayyari, F.; Wood, D. E.; Fanwick, P. E.; Sammelson, R. E. *Synthesis* **2008**, *2*, 279.
24. Zhu, X. Q.; Liu, Y. C. *J. Org. Chem.* **1998**, *63*, 2786.
25. Bagal, D. B.; Qureshi, Z. S.; Dhake, K. P.; Khan, S. R.; Bhanage, B. M. *Green Chem.* **2011**, *13*, 1490.
26. Gooben, L. J.; Ghosh, K. *Angew. Chem., Int. Ed.* **2001**, *40*, 3458.
27. Kumar, A.; Kumar, S.; Kapoor, K. K. *Aust. J. Chem.* **2007**, *60*, 621.
28. Zengin, M.; Genc, H.; Demirci, T.; Arslan, M.; Kucukislamoglu, M. *Tetrahedron Lett.* **2011**, *52*, 2333.