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Diastereoselective synthesis of *cis*-1,2-disubstituted cyclopropanols and cyclopent-3-enols via SmI_2 mediated C–N(Bt) bond cleavage

Tingting Xie, Liejin Zhou, Mengmeng Shen, Jianyong Li, Xin Lv *, Xiaoxia Wang *

Zhejiang Key Laboratory for Reactive Chemistry on Solid Surfaces, College of Chemistry and Life Sciences, Zhejiang Normal University, Jinhua 321004, People's Republic of China

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ABSTRACT

Diastereoselective synthesis of *cis*-1,2-disubstituted cyclopropanols and cyclopent-3-enols has been achieved from readily available β-benzotriazolyl ketones (β-Bt ketones) via a C–N(Bt) bond cleavage/cyclization process promoted by SmI_2/HMPA.

Introduction

Substituted cyclopropanols are important synthetic intermediates for their highly strained three-membered rings and can undergo regioselective C^1–C^3 or C^2–C^3 three-carbon bonds' cleavages to afford various functionalized compounds.[1] The cyclopropanol moiety exists in many biologically active compounds, which may be of medicinal or biological value.[2] For examples, several cyclopropanolamides (A) are potential drugs targeting cannabinoid and vanilloid receptors.[2a] It was reported that the (−)-bremazocine (B) acted as a k-opioid agonist[2b] and the cyclopropanol derivatives (C) were found to be medicinally useful as protein kinase inhibitors (Fig. 1).[2c]

Cyclopropanation of metal enolates may be a convenient method for the synthesis of cyclopropanols from ketones using Zn carbenoids,[3a–d] Mg carbenoids,[3e] or Sm carbenoids.[3f] However, the transformation of the ketones into the enolates may require strong bases and the diastereoselectivities are sometimes moderate. Kulinkovich hydroxycyclopropanation provides a flexible and convenient method for the synthesis of cyclopropanols from carboxylic esters in the presence of alkoxytitanium salt and Grignard reagent.[4] The reaction between carboxylic esters and styrenes on a Mg cathode could achieve a similar transformation to afford the cycloprapanols.[5] Brook rearrangement/cyclization of acylsilanes could generate 1,2-disubstituted

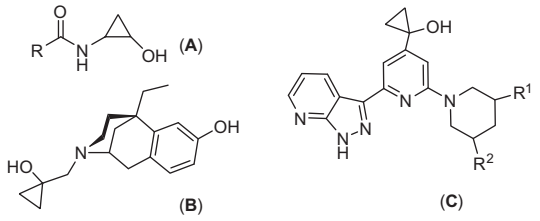

Figure 1. Several medicinally useful cyclopropanol derivatives.

cyclopropanols under basic conditions.[6] β,γ-Unsaturated carbonyl compounds underwent 3-exo-trig cyclizations mediated by SmI_2 providing an alternative access to cyclopraponals,[7] while the substrates require the conjugation of the alkene units with ester, cyano, and cyanophenyl group or aromatic moieties. Formation of cyclopropanols from α-haloketones[8a] or β-haloketones[8b] can also be achieved by SmI_2-mediated reactions with the stereochemistry either not mentioned or with moderate diastereoselectivity. Besides, 3-halo ketones were not readily available. Tsuchimoto group used 3-halo esters[8c] as the starting materials, wherein the 3-haloketones were transformed in situ and the 1-substituted cyclopropanols were prepared in excellent yields. However, the synthesis of 1,2-disubstituted cyclic alcohols using 3-halo esters is not known due to the availability of the starting 3-halo esters.

On the other hand, cyclopent-3-enols are subunits of many useful drugs or natural compounds.[9] For example, vibralactone and pactamycin both bear this scaffold with the former inhibiting

* Corresponding authors.
E-mail addresses: lvxin@zjnu.cn (X. Lv), wangxiaoxia@zjnu.cn (X. Wang).

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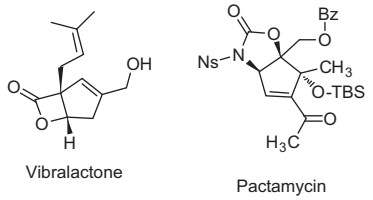


Figure 2. Natural products that bear cyclopent-3-enol scaffold.

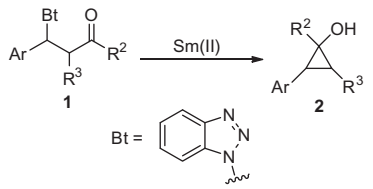
pancreatic lipase with an IC_{50} of 0.4 μg/mL[9a] and the latter being one of the well-known antibiotics (Fig. 2).[9d] Ring-closing of diallyl carbinols via olefin metathesis catalyzed by ruthenium(II) complexes afforded a facile access to the cyclopent-3-enol skeleton.[10] Conjugated dienes react with highly reactive magnesium to form the 1,3-diene-magnesium reagents, which on treatment with carboxylic acid esters at room temperature or reflux followed by workup afforded cyclopent-3-enols in excellent yields.[11] Interestingly, the electroreduction of a solution of 1,3-dienes and an aliphatic carboxylic ester with a Mg electrode also gives the enol in good yields.[5] Recently, conjugated dienes by coordination on Ti(II) complex when allowed to react with carboxylic esters at room temperature would lead to cyclopentenol derivatives in moderate yields.[12] Although the methods reported above are convenient and sometimes efficient, however, the stereochemistry of the cyclopent-3-enols was not involved.

Herein we wish to report SmI_2 mediated cleavage of C–Bt(benzotriazolyl) bond in the readily available β-Bt ketones for the diastereoselective synthesis of *cis*-1,2-disubstituted cyclopropanols and cyclopent-3-enols in good yields.

The properly located C–Bt bond could be readily cleaved by SmI_2. For example, the removal of a benzotriazolyl group from the α-benzotriazolyl ketones or *N*-acylbenzotriazoles was achieved by SmI_2 to afford the corresponding ketones[13a] or a-diketones.[13b] The elimination of a benzotriazolyl group from *N*-(α-amino)alkylbenzotriazoles,[13c,d] *N*-(α-benzotriazol-1-ylalkyl)amides and *N*-(α-benzotriazol-1-ylalkyl)-sulfonamides[13e] was readily realized with SmI_2 as a reducing agent. The resulting intermediates underwent either dimerization or cross-coupling reaction with carbonyl compounds, thus affording the corresponding dimers or α-hydroxyalkylated amines or sulfonamides. The benzotriazole adducts with an activated double bond underwent the reductive debenzotriazolylation in the presence of SmI_2 to produce an α-amino radical and subsequent intramolecular radical addition to the double bond afforded *N*-cycloalkylamines.[13f]

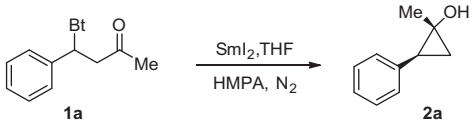
We envision the reductive cleavage of the C–Bt bond in β-benzotriazolyl ketones **1** would lead to an intramolecular cyclization and therefore provide a facile synthesis of substituted cyclopropanols **2** (Scheme 1).

In our initial studies, β-benzotriazolyl ketone **1a**, which could be facilely prepared from the Michael addition between 4-phenylbut-3-en-2-one and benzotriazole (BtH),[14] was added to the SmI_2/THF solution at room temperature. However, hardly any desired product was detected under the condition (Table 1, entry 1). Considering that the addition of HMPA[15] can enhance many reactions promoted by SmI_2, we then used it as an additive. In the presence of HMPA (4 equiv), the purple color faded away within several minutes and **1a** was completely consumed (monitored by TLC). Common work-up afforded the desired product **2a** in 27% yield (entry 2). Since the reaction was complicated and several by-products were detected, decrease of the temperature was applied. Slightly better results could be obtained at 0 °C (entry 3). However, further lowering the reaction temperature to −40 °C did not improve the result remarkably and longer reaction time was required (entries 4 and 5). Only trace amounts of **2a** could be obtained at −78 °C in 10 h (entry 6). The increase of the additive loading was then attempted. To our delight, the yield improved remarkably when 10 equiv of HMPA was added at ambient temperature (entry 7, 76% yield).



Scheme 1. Proposed SmI_2-mediated synthesis of substituted cyclopropanols.

Table 1
Optimization of reaction conditions for the SmI_2-promoted synthesis of 1-methyl-2-phenylcyclopropanol[a]



1a **2a**

Entry	The equiv of HMPA	Temperature (°C)	Time	Yield[b] (%)
1	0	rt	10 h	—[c]
2	4	rt	10 min	27
3	4	0	10 min	31
4	4	−30	20 min	35
5	4	−40	20 min	21
6	4	−78	10 h	Trace
7	10	rt	10 min	76

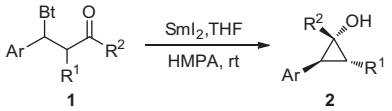
[a] Reaction conditions: substrate **1a** (1.0 mmol), SmI_2 (2.5 mmol) and HMPA in dry THF (15 mL) under N_2.
[b] Isolated yield.
[c] No reaction.

The phenyl and methyl groups in cyclopropano1 **2a** were assigned as *cis*- by ^{1}H NOE data, which revealed no NOE between the methyl substituent at C(1) and the benzylic H at C(2) on the cyclopropanol ring, and also by comparison with the reported spectra data for *cis*-1-methyl-2-phenylcycloprapanol.[4b] The reaction is highly diastereoselective since no formation of the other diastereomer could be detected by TLC analysis and crude ^{1}H NMR.

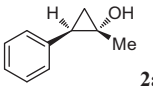
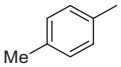
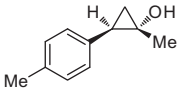
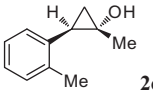
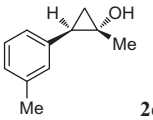
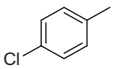
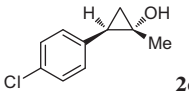
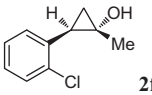
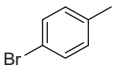
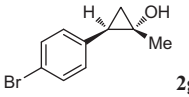
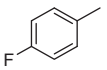
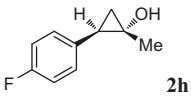
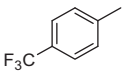
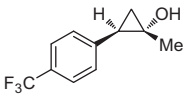
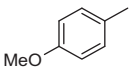
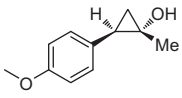
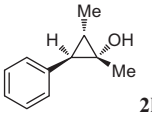
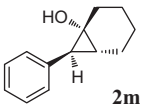
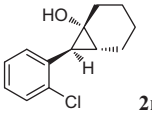
Under the optimal conditions established, we then examined the generality of the SmI_2-mediated cyclization by using a variety of β-benzotriazolyl ketones **1** (Table 2). Generally, the β-benzotriazolyl substrates reacted smoothly and gave the desired substituted cyclopropanols **2** in moderate to good yields within 10 min. Both electron-donating groups (Table 2, entries 2–4 and 10) and weak electron-withdrawing groups (entries 5–8 and 15) on the phenyl in R^1 were well tolerated. However, the substrates bearing strong electron-withdrawing groups such as $-CF_3$ gave the desired product only in poor yields (entries 9, 13 and 16). When R^2 was a phenyl (**1k**), the desired reaction failed (entry 11) and 1,3-diphenylpropan-1-one resulting from the simple reductive debenzotriazolylation was obtained almost quantitatively. The presence of α-methyl (**1l**) led to a sharp decrease in yield (entry 12), indicating the α-steric hindrance might affect the intramolecular cyclization process. However, when cyclized β-benzotriazolyl ketones **1n** and **1o** were used as the substrates, the reactions proceeded smoothly (entries 13 and 14). It is noteworthy that only one diastereomer of **2** was obtained for all the substrates tested.

We then sought to extend the protocol to synthesize structurally more versatile molecules. Interestingly, when **3a** was used

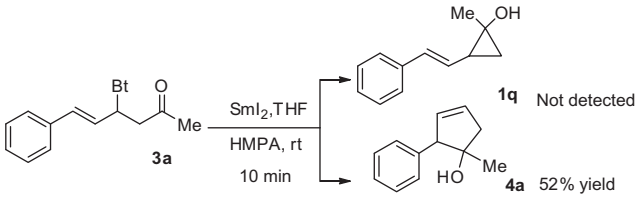
Table 2
SmI_2-mediated diastereoselective synthesis of substituted cyclopropanols from β-benzotriazolyl ketones[a]



1 2

Entry	Ar	R^1	R^2	Substrate **1**	Product **2**[b]	Yield[c] (%)
1		H	Me	**1a**	 **2a**	76
2		H	Me	**1b**	 **2b**	72
3		H	Me	**1c**	 **2c**	70
4		H	Me	**1d**	 **2d**	62
5		H	Me	**1e**	 **2e**	64
6		H	Me	**1f**	 **2f**	59
7		H	Me	**1g**	 **2g**	71
8		H	Me	**1h**	 **2h**	60
9		H	Me	**1i**	 **2i**	32
10		H	Me	**1j**	 **2j**	65
11		H	Ph	**1k**	**2k**	—[d]
12		Me	Me	**1l**	 **2l**	38
13		–$(CH_2)_4$–		**1m**	 **2m**	64
14		–$(CH_2)_4$–		**1n**	 **2n**	58

[a] Reaction conditions: substrate **1** (1.0 mmol), SmI_2 (2.5 mmol), and HMPA (10 equiv), in THF (15 mL) at room temperature (monitored by TLC) under N_2 for 10 min.
[b] Only one diastereomer was obtained. The relative configuration was assigned according to the values of ^3J coupling constants between the cyclopropyl protons (J = 6.3 Hz).[3b]
[c] Isolated yields.
[d] The desired product was not observed. 1,3-Diphenylpropan-1-one, resulting from simple reductive debenzotriazolylation and protonation, was isolated almost quantitatively.



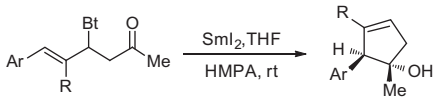
Scheme 2. The reaction of β-benzotriazolyl-β-alkenyl ketones **3a**.

as the substrate, which was incorporated with an additional C=C bond, cyclopent-3-enols **4a** was isolated in moderate yield instead of the expected **1q** (Scheme 2).

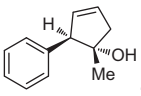
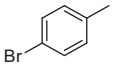
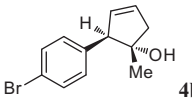
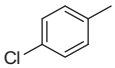
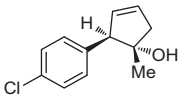
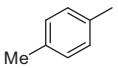
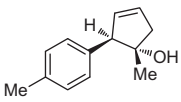
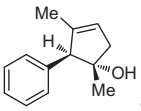
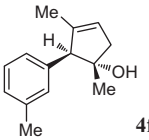
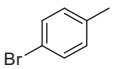
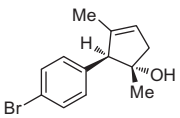
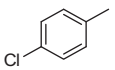
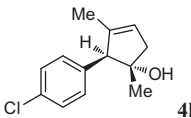
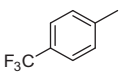
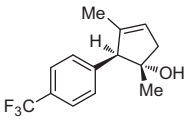
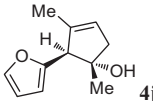
We further applied the same protocol in the synthesis of cyclopent-3-enols **4** using γ,δ-unsaturated β-benzotriazolyl ketones as the substrates and the results are listed in Table 3.

As shown in Table 3, the electron-donating and electron-withdrawing groups (such as Me, Br and Cl) on the phenyl were well

Table 3
SmI_2-mediated synthesis of substituted cyclopent-3-enols[a]



3 4

Entry	Ar	R	Substrate **3**	Time (min)	Product **4**	Yield[b] (%)
1		H	**3a**	10	 **4a**	52
2		H	**3b**	10	 **4b**	47
3		H	**3c**	10	 **4c**	51
4		H	**3d**	30	 **4d**	58
5		Me	**3e**	30	 **4e**	43
6		Me	**3f**	30	 **4f**	35
7		Me	**3g**	10	 **4g**	62
8		Me	**3h**	10	 **4h**	65
9		Me	**3i**	10	 **4i**	70
10		Me	**3j**	30	 **4j**	74

[a] Reaction conditions: substrate **3** (1.0 mmol), SmI_2 (2.5 mmol), and HMPA (10 equiv), in dry THF (15 mL) at room temperature (monitored by TLC) under N_2 substrate **1a** (1.0 mmol), SmI_2 (2.5 mmol) and HMPA in dry THF (15 mL) under N_2.
[b] Isolated yield.

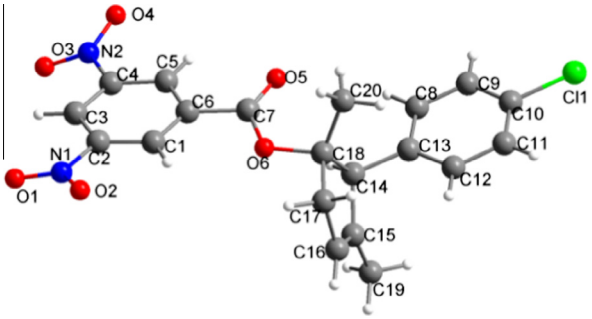
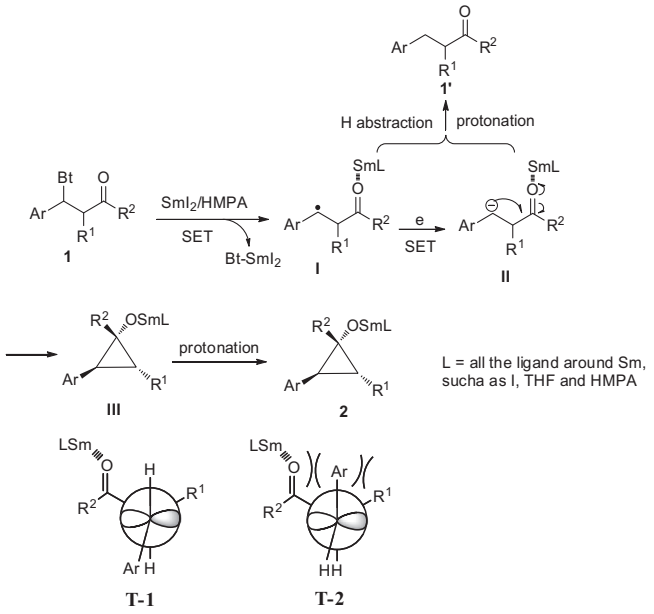


Figure 3. The X-ray crystal structure of **5a** (the 3,5-dinitrobenzoate of **4h**).



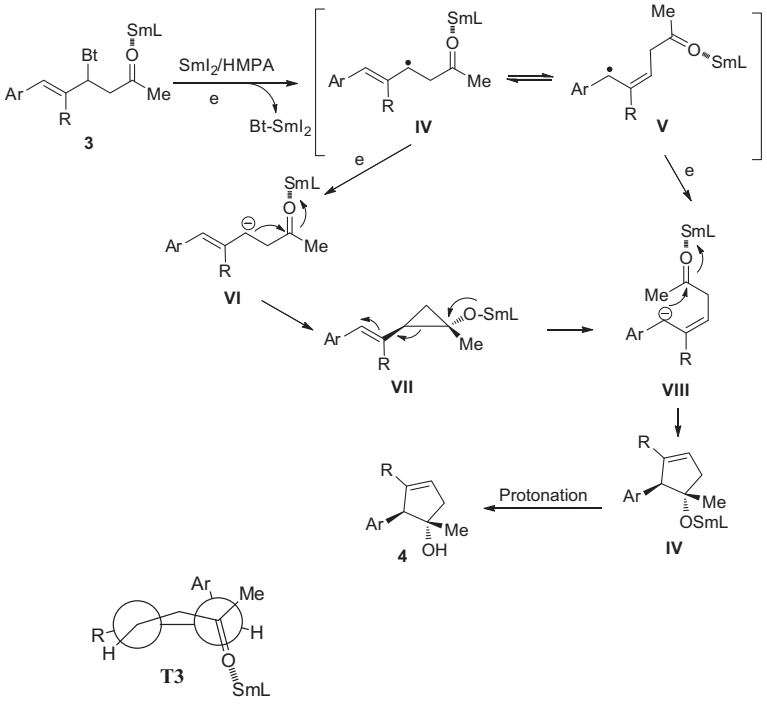
Scheme 3. Plausible mechanism for the SmI_2-mediated synthesis of cyclopropanols.

tolerated and moderate yields of the desired cyclopent-2-enols could be obtained within 10 min (Table 3, entries 1–10).

The transformation of **3** into products **4** were also completely diastereoselective as only one diastereomer was detected in all cases. The relative configuration of **4** was determined to be *cis*-1,2-dialkyl substitution by NOE studies. For product **4h** (R^1 = phenyl and R^2 = methyl), the *cis* structure was demonstrated by single-crystal X-ray crystallographic analysis of its 3,5-dinitrobenzoate **5a**, mp 165–167 °C (Fig. 3).[16]

In light of the excellent reducing ability of SmI_2,[17] a plausible single electron transfer (SET) mechanism for the formation of cyclopropanols is proposed as shown in Scheme 3. First, SmI_2 reacts with β-benzotriazolyl ketones **1** through a C(sp^3)–N(Bt) cleavage process to form a benzyl radical intermediate **I** along with a benzotriazolyl Sm(III) complex (Bt-SmI_2); a second electron transfer from SmI_2 to the benzyl radical generates carbanion **II**, which then undergoes intramolecular attack on the carbonyl to afford the cyclopropanol skeleton **III**. Reductive removal of Bt occurs prior to the reduction of the carbonyl was supported by the isolation of the simple ketone **1′** as a by-product (see Supporting information). Protonation of **III** will afford the final product **2**. The transformation from **II** into **III** is stereoselective and may be rationalized by the transitional state **T1** with the least repulsion between the aromatic ring, the carbonyl, and R^1. The formation of the other diastereomer was not observed, which would otherwise be generated via the energetically unfavorable **T2**.

The proposed SET mechanism may also account for the formation of cyclopent-3-enol derivatives **4**. As depicted in Scheme 4, β-benzotriazolyl ketones **3** accept an electron (e) from SmI_2 to give a radical intermediate **IV**. **IV** may rearrange to form a more stable benzyl radical **V** followed by a second electron transfer to transform into carbanion **VIII**. Alternatively, **IV** may also accept another electron to become carbanion **VI**. Intramolecular cyclization of **VI** generates vinyl substituted cyclopropanol samarium salt **VII**, which should be susceptible to rearrangement into **VIII** and finally affords cyclopentenol skeleton **IV**.[11,18] The desired product **4** could be obtained after the hydrolysis. The formation of transition state **T3** may account for the stereoselective transformation of **VIII** into



Scheme 4. Possible mechanism for the SmI_2-mediated synthesis of cyclopent-2-enols.

IV. Similar to the Cram's rule, the carbonyl tend to be *anti* periplanar to the large aryl group in the transitional state, thus would result in the *cis*-1,2-disubstituted cyclopent-3-enols.

In summary, we have developed a facile and diastereoselective synthesis of *cis*-1,2-disubstituted cyclopropanols and cyclopent-3-enols from β-benzotriazolyl ketones via the SmI_2 mediated C–N cleavage/cyclization process.[19] The readily available materials, high stereoselectivity, and mild conditions could make the present method practical and attractive.

Acknowledgments

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Supplementary data

Supplementary data (the spectral data and the ^1H NMR, ^{13}C NMR spectra of new substrates **1** and **3**, the products **2** and **4**; the crystal data of **5a**) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2015.05.002.

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19. *General Procedure for the Synthesis of Cyclopropanols* (**2**) and cyclopent-3-enols (**4**). An oven-dried 50 mL two-necked flask containing finely powdered samarium (0.375 g, 2.5 mmol) was evacuated and backfilled with N_2 for three times. Under a positive pressure of nitrogen, a solution of iodine (0.635 g, 2.5 mmol) in dry THF (12 mL) was added via a syringe. The mixture was allowed to stir at room temperature for 1 h. HMPA (2 mL) was then added followed by addition of a solution of substrate **1** or **3** (1 mmol) in dry THF (3 mL) via a syringe. The reaction mixture was stirred at room temperature until the completion of the reaction (monitored by TLC). The reaction was quenched by a satd potassium sodium tartrate solution (15 mL). The mixture was extracted by ethyl ether (3 × 15 mL). The combined extracts were washed with brine (15 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel (300–400 mesh) using petroleum/EtOAc (5:1, v:v) as eluent to afford the corresponding product **2** or **4**.
Selected spectral data of the products:
cis-1-Methyl-2-phenylcyclopropanol (**1a**). Yello oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.30–7.14 (m, 5H), 2.36 (dd, J = 10.0, 7.2 Hz, 1H), 2.01 (br s, 1H), 1.26 (dd, J = 10.2, 5.9 Hz, 1H), 1.20 (s, 3H), 0.99 (t, J = 6.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.6, 128.4, 128.2, 126.0, 57.5, 30.7, 20.7, 18.9.
cis-1-Methyl-2-phenylcyclopent-3-enol (**4a**), Yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.33–7.28 (m, 2H), 7.27–7.21(m, 1H), 7.22–7.13 (m, 2H), 5.99 (dd, J = 4.1, 1.8 Hz, 1H), 5.88 (dd, J = 4.1, 1.8 Hz, 1H), 3.79 (s, 1H), 2.53 (s, 2H), 2.06 (br s, 1H), 0.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.0, 133.2, 130.2, 128.3, 128.2, 126.7, 82.2, 63.8, 47.8, 25.0. HRMS (ESI) m/z: calcd for $C_{12}H_{13}$ $[M-H_2O+H]^+$: 157.1017; found: 157.1011.