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ARTICLE

β-Cyclodextrin in water: Highly facile biomimetic one pot deprotection of phenolic THP/MOM/Ac/Ts ethers and concomitant regioselective cyclization of chalcone epoxides and 2'-aminochalcones

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A mild and efficient one-pot deprotection of THP/MOM/Ac/Ts ethers and concomitant cyclization of chalcone epoxides to 2-hydroxyindanones and 2'-aminochalcones to aza-flavanones using β-Cyclodextrin in water has been developed. β-CD was found to be highly effective in carrying out deprotection and sequel transformations under eco-friendly environment affording moderate to excellent yields (59-99%) at 60 ^{o}C in 8-22 min. Water, an eco-friendly reaction medium, has been utilized for the first time in this reaction. The merits of the presented protocol include high yields, catalyst reusability and preclude use of metals and organic solvents. The present method is very much milder but more advanced than those reported earlier.

Introduction

Protection and deprotection of hydroxyl groups have fundamental importance and most frequently used strategies in the multi-steps organic syntheses. In particular, these two phenomena are extremely important because of their presence in a number of natural products, biological and synthetic compounds such as carbohydrates, peptides, macrolides, nucleotides, steroids and polyethers.[1] Among the various methods for protecting hydroxy group, the formation of tetrahydropyranyl ethers (THPEs) is the most commonly employed methods due to its easy formation and inertness to various reaction conditions like strong bases such as metal hydrides, organolithium compounds, Grignard reagents, catalytic hydrogenation and alkylating or acylating conditions.[2] Likewise, methoxymethyl chloride (MOMCl), acetyl chloride/acetic anhydride (CH_3COCl/Ac_2O) and tosyl chloride (TsCl) are also important reagents for the alcoholic and phenolic group protection. Various methods have been reported for the deprotection of THPEs that include protic acids,[3a-d] BF_3–etherate,[3e] LiBr,[3f] LiOTf,[3g] $LiBF_4$,[3h] $LiClO_4$,[3i] $In(OTf)_3$,[3j] $Sc(OTf)_3$,[3k] I_2,[3l] $InCl_3$,[3m] $ZrCl_3$,[3n] $CuCl_2$,[3o] NH_4Cl,[3p] and other catalysts. Similarly, Many catalysts have been used to remove MOM group under acidic conditions such as using protic acids,[4a] Lewis acids,[4b] Lewis acid-thiol,[4c] boron halides,[4d] $YbCl_3$,[4e] CBr_4-PPh_3,[4f] $ZnBr_2$,[4g] silica-supported $NaHSO_4$,[4h] and TMSOTf (TESOTf)-2,2'-bipyridyl.[4i] Several catalysts have been reported for the deacetylation and detosylation of alcohols and phenols under acidic and basic conditions including NaOMe,[5a] micelles,[5b] Zn-MeOH,[5c] enzymes,[5d] metallo-enzyme,[5e] metal complexes,[5f] antibodies,[5g] montmorillonite K-10,[5h] I_2,[5i] $NaBO_3$,[5j] and TFA.[5k] Most of these methods, however have one or other drawbacks such as low yields, long reaction times, reflux at high temperature, excess amounts of reagents and tedious workup procedures.[6] Hence, there is still scope to develop milder and efficient methods in the detetrahydropyranylation, demethoxymethylation, deacetylation and detosylation of hydroxyl groups.

Similarly, various reagents and reaction conditions have been previously employed for the cyclization of chalcones to aza-flavanones such as acids,[7a] bases,[7b-d] silica gel,[7e-g] light,[7h] electrolysis,[7i] nanocrystalline MgO,[7j] zeolites,[7k] L-Proline,[7l] $Yb(OTf)_3$,[7m-n] silica gel supported $TaBr_5$,[7o] alumina supported-$CeCl_3.7H_2O$-NaI,[7p] and microwave.[7q-r] Most of these procedures however have drawbacks for example low yields, use of toxic metals and organic solvents and harsh reaction conditions.

Therefore, in metal free green context, cyclodextrins are emerging as alternative catalyst for numerous challenging organic reactions due to their fine tuning of their physico-chemical properties.[8-10] Cyclodextrins (CDs), which are cyclic oligosaccharides possessing hydrophobic cavities, exert microenvironmental effects leading to selective reactions. They catalyze reactions by supramolecular catalysis through non-covalent bonding forming reversible host-guest complexes just like in enzymes. We used β-Cyclodextrin as the catalyst because it is easily accessible and inexpensive among the CDs. The concept of green chemistry has attracted the attention of performing reactions in aqueous medium. However the fundamental problem in performing the organic reactions in water is that many organic substrates are hydrophobic and are insoluble in water. But this can be overcome by the use of cyclodextrins.[11]

As a continuation of our recent findings of $YbCl_3$-catalyzed ring-opening of epoxides[4e] herein, we report a simple and efficient green protocol for the biomimetic one pot deprotection of MOM/THP/Ac/Ts ethers and also the concomitant regioselective cyclization of chalcone epoxides to 2-hydroxyindanones and 2'-

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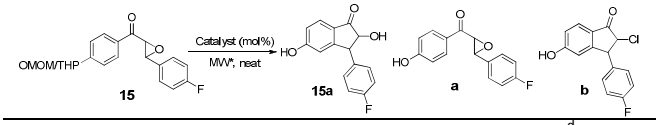
aminochalcones to aza-flavanones employing a mild and environmentally friendly catalyst β-CD in water as a novel reagent under microwave condition. These 2-hydroxyindanones and aza-flavanones are widely used as synthetic intermediates of high significance in organic and medicinal chemistry.

Results and discussion

In our initial study toward the development of this methodology, a model reaction was conducted by treating the substrate **15** in the presence of various metal salts and then finally β-cyclodextrin. Initially, the catalytic efficiency of different Lewis acids ($CdCl_2$, $CoCl_2$, $FeCl_3$, $ZnCl_2$, $SrCl_2$, $CuCl_2$, NH_4Cl, CuI_2, $InCl_3$, $HgCl_2$, $SnCl_2.2H_2O$ and $CeCl_3$) was screened (Table 1).

The metal halides such as $CdCl_2$, $CoCl_2$, $FeCl_3$ and $ZnCl_2$ did not show any catalytic activity in the formation of product **15a** instead yielded the side product **b** in excellent yields (Table 1, entries 1-4). $SrCl_2$ was unable to give any of the products (Table 1, entry 5). $CuCl_2$ yielded only the deprotected product **a** without cyclization in good yield (Table 1, entry 6). The Lewis acids like NH_4Cl, CuI_2 and $InCl_3$ exhibited poor to moderate catalytic activity at 10 mol % catalyst loading furnishing the product **15a** in 5-67% yields with the formation of side products **a** and **b** also (Table 1, entries 7-9). The $HgCl_2$, $SnCl_2.2H_2O$ and $CeCl_3$ were found to be the good catalyst at 10 mol% catalyst loading, which gave 55-75% yields of product **3b** without forming any side products within 4-10 min (Table 1, entries 10-12). Then, the catalyst optimization was achieved for the catalyst β-cyclodextrin in water.

Table 1. Optimization of reaction conditions for deprotection and concomitant cyclization of chalcone epoxide.

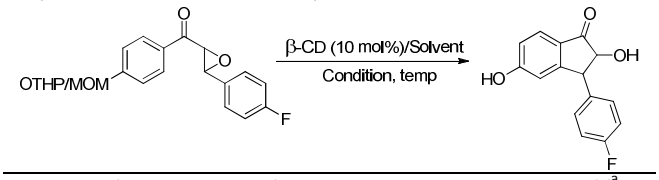


Entry	Catalyst	Mol%	Temp (^{0}C)	Time (min)	Yield[d] (%)		
					15a	**a**	**b**
1	$CdCl_2$	10	40	4	-	-	90
2	$CoCl_2$	10	40	2	-	-	94
3	$FeCl_3$	10	40	2	-	-	93
4	$ZnCl_2$	10	40	2	-	-	91
5	$SrCl_2$	10	40	10	-	-	-
6	$CuCl_2$	10	40	10	-	84	-
7	NH_4Cl	10	40	10	5	55	-
8	CuI_2	10	40	5	20	40	-
9	$InCl_3$	10	40	5	67	10	20
10	$HgCl_2$	10	40	5	55	-	-
11	$SnCl_2.2H_2O$	10	40	10	58	-	-
12	$CeCl_3$	5	40	4	75	-	-
13[c]	β-CD	20	60	10	95	-	-
14[c]	**β-CD**	**10**	**60**	**10**	**95**	**-**	**-**
15[c]	β-CD	5	80	20	65	-	-

Reaction was carried out on a 1 mmol scale; *Anton Paar Monowave-300 reactor®; H_2O was used as solvent for entry 13-15; [d]Isolated yields.

To optimize the catalyst loading, three consecutive reactions were carried out in 20, 10 and 5 mol% catalyst loadings under microwave irradiation (Tables 1, entries 13-15). The reaction proceeded smoothly with β-cyclodextrin in water at 20 and 10 mol% catalyst loading with the same capacity providing the product **15a** (deprotection with cyclization) in 95% yield (Tables 1, entries 13, 14), but further decreasing the catalyst loading to 5 mol% furnished the product **15a** in only 65% yield even after prolonging the reaction time and temperature (Tables 1, entry 15).

Table 2. Optimization of the solvent and reaction time on yields of deprotection and concomitant cyclization.



Entry	Solvent	Condition	Temp (^{0}C)	Time (min)	Yield[a] (%)
1	Acetonitrile	MW[b]	70	15	32
2	DCM	MW[b]	40	13	51
3	THF	MW[b]	65	10	55
4	Acetone	MW[b]	55	12	63
5	DMF	MW[b]	80	8	71
6	DMSO	MW[b]	80	10	88
7	**H_2O**	**MW[b]**	**60**	**10**	**99**
8	H_2O	MW[b]	60	8	89
9	H_2O	CH[c]	60	5h	81

Reaction was carried out on a 1 mmol scale; [a]Isolated yields.

We also screened solvents like acetonitrile, CH_2Cl_2, THF, acetone, DMF, DMSO and neat H_2O where solvents like CH_2Cl_2, THF, acetone, DMF and DMSO gave good results (Table 2, entries 2-6). However, neat H_2O was found to give the best results with quantitative conversion (99%) at 60 ^{0}C under microwave irradiation. Despite the excellent results, we further explored other reaction conditions for the above reaction in order to target the optimum protocol for the transformation. For example, the reaction was subjected to conventional heating also, however it resulted in 81% yield of the product (Table 2, entry 9) in 5h. The advantages of use of microwave irradiation over conventional heating helped in the reduction in reaction time from hours to minutes. Hence, the optimum conversion of substrates **15** to product **15a** was attained when the reaction was carried out by utilising 10 mol % β-cyclodextrin in water at 60 ^{0}C for 10 min under microwave condition.

Then, under optimal reaction condition, we carried out reactions of deprotection of various phenolic and alcoholic THP/MOM/Ac/Ts ethers and concomitant ring opening of chalcone epoxides using β-cyclodextrin in water (Table 3). The reaction underwent deprotection and sequel cyclization in excellent yields for detetrahydropyranylation, demethoxymethylation and deacetylation (92–99%) but in moderate yields for detosylation (61–74%) within 8-9 min at 60 ^{o}C (Table 3, entries 1–9). In case of chalcones (**5-14**), only deprotection was observed without cyclization. Interestingly, the deprotection of THP/MOM ethers followed by the Friedel–Crafts alkylation was observed for the chalcone epoxides (**15-21**) giving the corresponding 2-hydroxyindanones (**15a-21a**) in excellent yields (95–99%) within 10 min. We also subjected alicyclic tetrahydropyranyl tosylates (**22-26**) to the same reaction protocol which resulted in moderate yields (59–63%) of their respective products (**22a-26a**) in 14-15 min. All the synthesized products were characterized by mass, FTIR, NMR and also comparing with the available literature.[4e, 5k]

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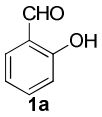
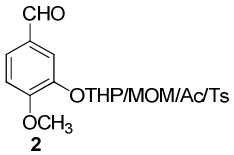
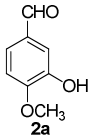
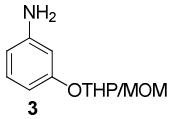
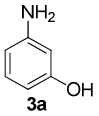
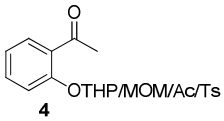
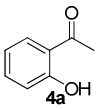
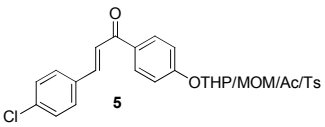
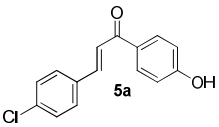
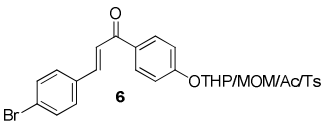
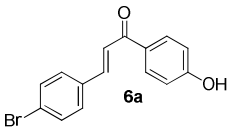
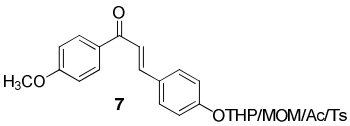
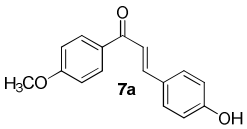
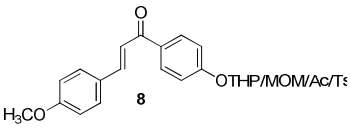
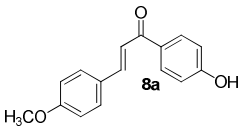
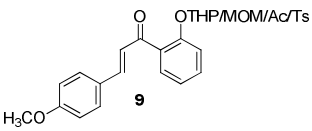
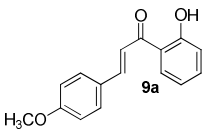
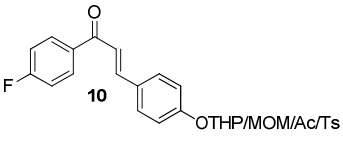
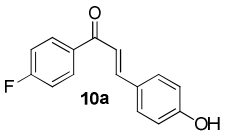
Table 3. β-CD mediated one pot deprotection and sequel cyclization of chalcone epoxides under MW condition.

Entry	Substrate	Product	Time (min)	Yields (%)			
				a	b	c	d
1			8	99	99	99	73
2			9	99	99	99	70
3			8	99	98	-	-
4			8	98	97	99	61
5			8	95	94	97	68
6			8	95	94	98	72
7			8	96	95	94	70
8			8	93	95	94	67
9			8	95	94	97	69
10			8	93	92	97	70

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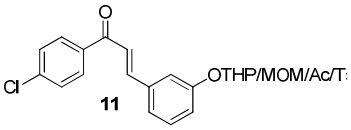
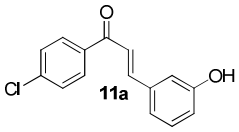
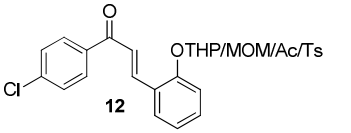
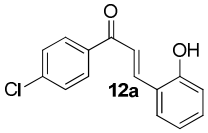
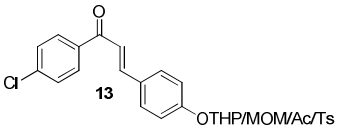
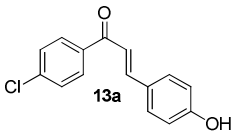
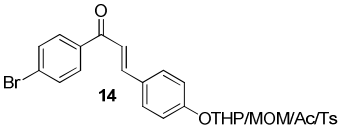
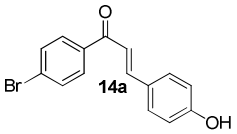
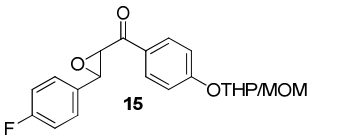
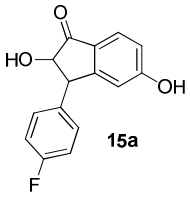
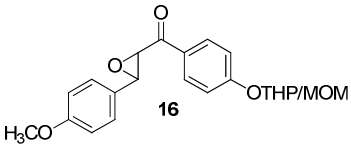
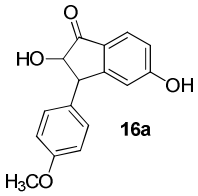
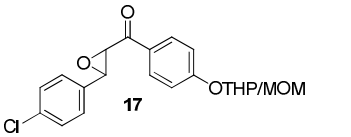
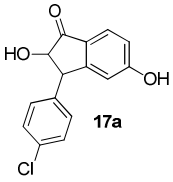
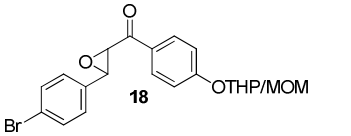
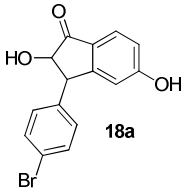
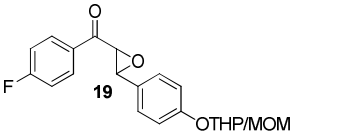
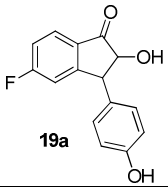
11			8	95	93	95	72
12			8	96	92	93	72
13			8	93	97	94	74
14			8	95	98	97	71
15			10	99	99	-	-
16			10	99	98	-	-
17			10	98	99	-	-
18			10	96	97	-	-
19			10	98	95	-	-

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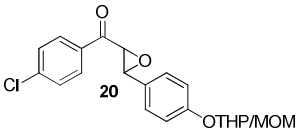
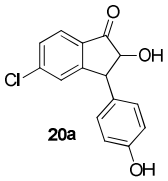
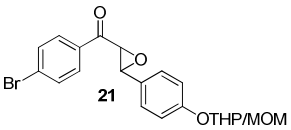
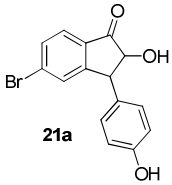
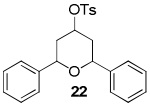
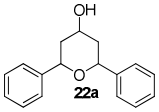
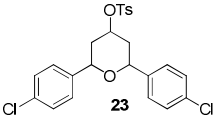
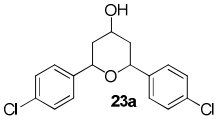
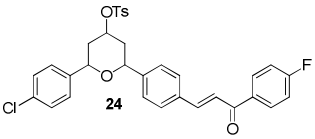
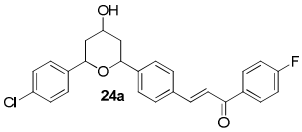
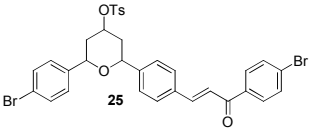
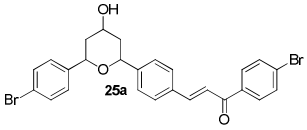
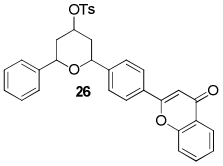
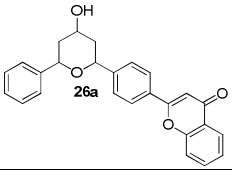
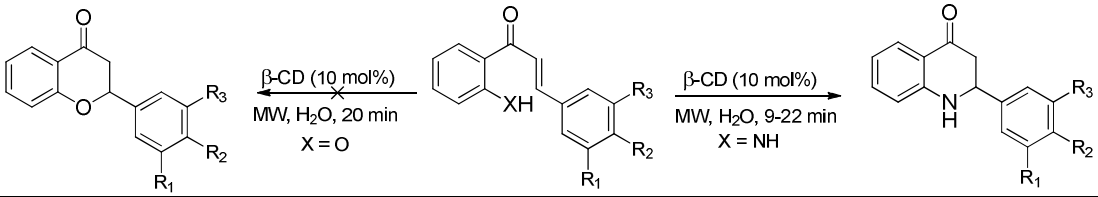
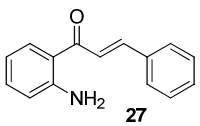
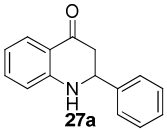
20			10	96	95	-	-
21			10	99	97	-	-
22			14	-	-	-	62
23			14	-	-	-	60
24			14	-	-	-	61
25			15	-	-	-	59
26			15	-	-	-	63

Reactions were carried out on a 1 mmol scale at 60 ^{0}C under MWI, β-CD (10 mol %); [a,b,c,d] Isolated yields from OTHP, OMOM, OAc and OTs respectively.

The scope of β-cyclodextrin as catalyst was also tested for the cyclization of 2'-aminochalcones (**27-36**) to their corresponding aza-flavanones (**27a-36a**). Under optimal reaction conditions, β-cyclodextrin catalyzed the isomerization of 2'-aminochalcones to their corresponding aza-flavanones in excellent yields (70-96%) within 9-22 min (Table 4).

Table 4. β-CD mediated one pot deprotection and concomitant cyclization of 2'-aminochalcones under MW condition.



Entry	Substrate	Product	Time (min)	Yield (%)
1			15	96

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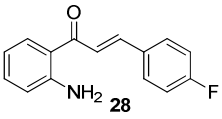
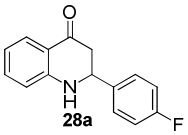
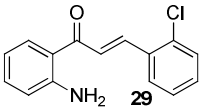
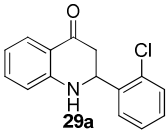
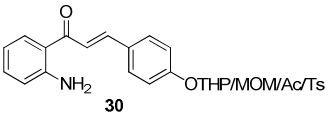
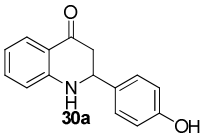
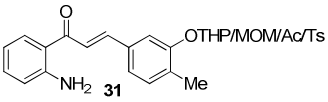
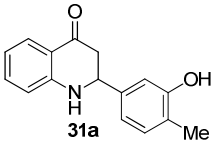
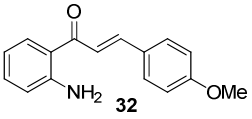
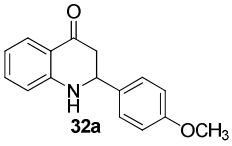
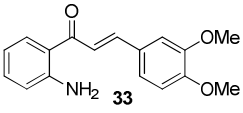
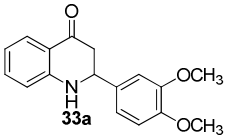
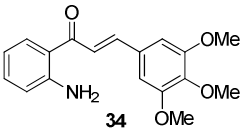
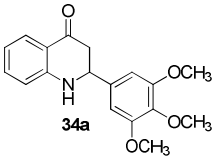
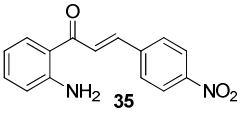
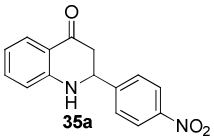
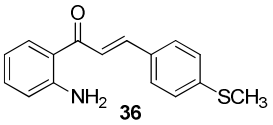
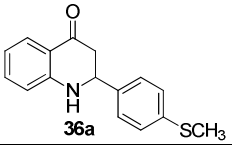
2	 **28**	 **28a**	20	90
3	 **29**	 **29a**	18	92
4	 **30**	 **30a**	20	93[a], 92[b], 95[c], 70[d]
5	 **31**	 **31a**	20	88[a], 90[b], 94[c],73[d]
6	 **32**	 **32a**	10	96
7	 **33**	 **33a**	9	95
8	 **34**	 **34a**	9	93
9	 **35**	 **35a**	22	81
10	 **36**	 **36a**	12	89

Reactions were carried out on 1 mmol scale at 60 °C under MWI, β-CD (10 mol %); [a,b,c,d] Isolated yields from OTHP, OMOM, OAc and OTs respectively.

In addition, we also studied the substituents effects of electron-donating to electron-withdrawing groups of Ar^2 ring of 2'-aminochalcones on the reaction rate and product yields. As anticipated, electron donating groups enhanced the cyclization to give the corresponding aza-flavanones in good yields while electron withdrawing groups slow down the cyclization leading to moderate yields of aza-flavanones. For example, electron-donating groups such as $–CH_3$, OCH_3 and $–SCH_3$ groups on Ar^2 afforded the product in excellent yields at a faster rate (Table 2; **32a-34a**, **36a**). The substituents such as -F and -Cl on Ar^2 furnished the corresponding products in excellent yields (90-92%) but took longer reaction time (Table 2; **28a**, **29a**). Similarly, electron-withdrawing group such as $–NO_2$ on Ar^2 gave product in 81% yields and took longer reaction time (Table 2; **35a**). In case of cyclization of 2'-hydroxychalcones to their corresponding oxa-flavanones, reaction didn't proceed and this might be due to poor nucleophilicity of the hydroxyl group under similar reaction conditions.

All the isolated products were confirmed by their IR, ^{1}H NMR spectral analysis and with available literature data.[7o-p] For example, the ^{1}H-NMR spectrum of *2-(3,4-dimethoxyphenyl)-2,3-dihydroquinolin-4(1H)-one* **33a** shows a doublet of doublets at 5.43 ppm due to -CH proton at 2- position and 2 doublet of doublets (dd) at 2.88-3.13 ppm due to $-CH_2$ proton at 3-position which is the characteristic of flavanone and peak of one H at 12.17 ppm due to -NH is in agreement with cyclization of 2'-aminochalcone to aza-flavanone.

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A plausible reaction mechanism for the THP ether deprotection and the simultaneous intramolecular Friedel–Crafts alkylation is depicted in scheme 1. The role of β-CD appears to be not only to activate the THP ether and epoxide by hydrogen bonding but also to promote highly regioselective ring opening from β-carbon due to considerable electron deficient character at the benzylic position not on α-carbon due to a 4-membered cyclobutanone (unstable intermediate, Route-2) (Fig. 1). Therefore, route 1 was preferred to route 2 because of stable carbocation formation and the nucleophilic attack took place at the β-carbon because of better resonance stabilized benzal intermediate which resulted in faster epoxide ring opening from β-carbon resulting in a five membered ring which on subsequent hydrolysis gave the desired product with concurrent liberation of β-CD for next catalytic cycle. In these reactions, β-CD was recycled and reused.

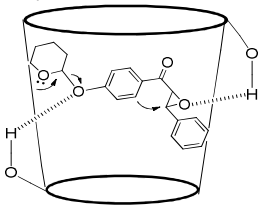
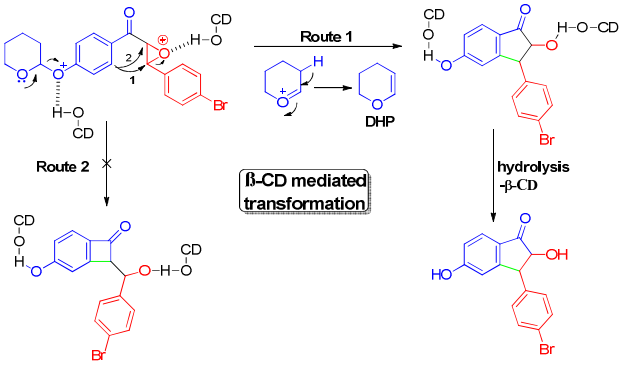


Fig. 1 Mechanistic Rationale of β-cyclodextrin induced deprotection of phenolic ether and concomitant cyclization.



Scheme 1. Plausible reaction mechanism of β-cyclodextrin induced deprotection of phenolic THP ether and concomitant intramolecular Friedel–Crafts alkylation.

Conclusions

Thus, we have developed for the first time the successful use of β-cyclodextrin in water for the deprotection of THP/MOM/Ac/Ts ethers and concomitant regioselective ring opening of chalcone epoxides via intramolecular Friedel-Krafts alkylation to produce 2-hydroxyindanones and cyclization of 2'-aminochalcone to aza-flavanone under supramolecular catalysis affording the products in excellent yields (59–99%) within 8-22 min and therefore represent a novel methodology. This high regioselectivity was achieved due to the inclusion complex formation of epoxides with β–CD. This method precludes the use of organic solvents, toxic metals, acid or base catalysts. Some important features of the method include high yields, shorter reaction time, green conditions, reusability of catalyst and easy workup.

Experimental

All the required chemicals were purchased from Merck and Aldrich Chemical Company. Pre-coated aluminium sheets (silica gel 60 F254, Merck) were used for thin-layer chromatography (TLC) and spots were visualized under UV light. Silica gel column chromatography was performed using silica gel 60–120 mesh size (RANKEM Limited). IR spectra were recorded with KBr on Thermo Nicolet FT-IR spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on Jeol ECX 400 MHz and Bruker Spectrospin DPX 500 MHz spectrometer using $CDCl_3$ as a solvent and trimethylsilane (TMS) as an internal standard. Spectra were processed using Bruker Topspin® 3.0.b.8. Splitting patterns are designated as follows; s = singlet, d = doublet, dd = doublets of doublet, m = multiplet, br = broad. Chemical shift (δ) values are given in ppm. Mass spectra were collected using a direct inlet system (70 eV) with a VL detector (ES, 4000 V) on Perkin Elmer GC-MS. High-resolution mass spectra (HRMS) were obtained on a Brüker micrOTOF™-Q II mass spectrometer (ESIMS).

Microwave Irradiation Experiment. All microwave experiments were carried out in a dedicated Anton Paar Monowave-300 reactor®, operating at a frequency of 2.455 GHz with continuous irradiation power of 0 to 850 W. The reactions were performed in a G-30 Borosilicate glass vial sealed with Teflon septum and placed in a microwave cavity. Initially, microwave of required power was used and temperature was being ramped from room temperature to a desired temperature. Once this temperature was attained, the process vial was held at this temperature for required time. The reactions were continuously stirred. Temperature was measured by an IR sensor. After the experiments a cooling jet cooled the reaction vessel to ambient temperature.

General procedure for the microwave-assisted deprotection of THP, MOM, acetyl and tosyl ethers and concomitant cyclization of chalcone epoxides and 2'-aminochalcones: The substrate (1 mmol) dissolved in water (2 mL) was added to an aqueous solution of β-cyclodextrin (10 mol % in 10 mL of water) kept in a G-30 process vial and capped with Teflon septum. After a pre-stirring for one minute, the vial was subjected to microwave irradiation with the holding temperature of 60 °C for the prescribed time (Table 3 and 4). After completion of reaction, the mixture was cooled to room temperature and extracted with EtOAc (3 × 15 mL) and the catalyst was filtered off and washed with EtOAc (2×10 ml), filterate was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography using hexane/ethyl acetate (8:2) as an eluent if required otherwise compounds were pure enough for the spectral elucidation.

Characterization data for representative compounds:

(E)-3-(4-chlorophenyl)-1-(4-hydroxyphenyl)prop-2-en-1-one (**5a**): ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.99 (d, *J* = 8 Hz, 2H), 7.77 (d, *J* = 15.5 Hz, 1H), 7.63 (t, *J* = 8Hz, 2H), 7.46 (d, *J* = 15.5 Hz, 1H), 7.10 (t, *J* = 8.5 Hz, 2H), 6.95 (d, *J* = 8 Hz, 2H), 5.38 (s, 1H, D_2O exchangeable). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 186.88, 162.05, 141.32, 131.41, 130.90, 130.83, 128.92, 121.85, 115.81, 115.21. IR (KBr, ν_{max} = cm^{-1}): 3410, 2926, 2875, 1686, 1599, 1265, 1078, 862, 730. GC-MS (m/z): 302 [$M^{+\cdot}$, $C_{15}H_{11}BrO_2$], 304 [M+2].

(E)-3-(4-bromophenyl)-1-(4-hydroxyphenyl)prop-2-en-1-one (**6a**): ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.99 (d, *J* = 8 Hz, 2H), 7.77 (d, *J* = 15.5 Hz, 1H), 7.63 (t, *J* = 8Hz, 2H), 7.46 (d, *J* = 15.5 Hz, 1H), 7.10 (t, *J* = 8.5 Hz, 2H), 6.95 (d, *J* = 8 Hz, 2H), 5.48 (s, 1H, D_2O exchangeable). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 186.88, 162.05, 141.32, 131.41, 130.90, 130.83, 128.92, 121.85, 115.81, 115.21. IR (KBr, ν_{max} = cm^{-1}): 3410, 2926, 2875, 1686, 1599, 1265, 1078, 862, 730. GC-MS (m/z): 302 [$M^{+\cdot}$, $C_{15}H_{11}BrO_2$], 304 [M+2].

(E)-3-(4-hydroxyphenyl)-1-(4-methoxyphenyl)prop-2-en-1-one (**7a**): ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 8.03 (d, *J* = 8 Hz, 2H), 7.74 (d,

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J = 15.5 Hz, 1H), 7.56 (d, *J* = 8.5 Hz, 2H), 7.51 (d, *J* = 16 Hz, 1H), 7.38 (d, *J* = 8.5 Hz, 2H), 6.98 (d, *J* = 9 Hz, 2H), 5.48 (s, 1H, D_2Oexchangeable), 3.89 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 188.2, 163.9, 142.7, 131.4, 131.3, 130.1, 121.5, 116.8, 116.6, 114.2, 55.1. IR ν_{max} (KBr, cm^{-1}): 3410, 2928, 2880, 1684, 1599, 1265. GC-MS (m/z): 254 [M^+, $C_{16}H_{14}O_3$].

(E)-1-(4-hydroxyphenyl)-3-(4-methoxyphenyl)prop-2-en-1-one (**8a**): ^1H NMR ($CDCl_3$, 500 MHz, ppm) δ 8.03 (d, *J* = 8 Hz, 2H), 7.77 (d, *J* = 16 Hz, 1H), 7.55 (d, *J* = 8Hz, 2H), 7.42 (d, *J* = 15.5 Hz, 1H), 6.98 (d, *J* = 8 Hz, 2H), 6.89 (d, *J* = 8 Hz, 2H), 5.82 (s, 1H, D_2O exchangeable), 3.89 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 188.7, 163.6, 142.8, 131.2, 131.0, 130.4, 121.7, 116.3, 116.2, 114.0, 55.7. IR (KBr, ν_{max} = cm^{-1}): 3410, 2926, 2875, 1686, 1599, 1265. GC-MS (m/z): 254 [M^+, $C_{16}H_{14}O_3$].

(E)-1-(2-hydroxyphenyl)-3-(4-methoxyphenyl)prop-2-en-1-one (**9a**): ^1H NMR ($CDCl_3$, 400 MHz, ppm) δ 7.91-7.86 (m, 2H), 7.61 (d, *J* = 8.8 Hz, 2H), 7.52 (d, *J* = 15.6 Hz, 1H), 7.49-7.45 (m, 2H), 7.00 (dd, *J* = 1.2, 8.8 Hz, 1H), 6.93 (d, *J* = 8.4 Hz, 2H), 3.84 (s, 3H), 1.68 (s, 1H, D_2O exchangeable). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 193.8, 163.7, 162.1, 145.5, 136.3, 130.7, 129.7, 127.4, 120.2, 118.9, 118.7, 117.7, 114.6, 55.6. IR (KBr, ν_{max} = cm^{-1}): 3410, 2926, 2875, 1686, 1599, 1265. GC-MS (m/z): 254 [M^+, $C_{16}H_{14}O_3$].

(E)-1-(4-chlorophenyl)-3-(2-hydroxyphenyl)prop-2-en-1-one (**12a**): ^1H NMR ($CDCl_3$, 400 MHz, ppm) δ 7.92-7.84 (m, 2H), 7.64-7.58 (m, 3H), 7.53-7.49 (m, 1H), 7.41 (d, *J* = 8.8 Hz, 2H), 7.01 (d, *J* = 8.4 Hz, 1H), 6.95 (d, *J* = 7.2 Hz, 2H), 4.84 (s, 1H, D_2O exchangeable). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 193.6, 163.8, 144.1, 136.7, 133.2, 131.7, 130.0, 129.8, 129.5, 129.0, 120.7, 119.1, 118.9. IR (KBr, ν_{max} = cm^{-1}): 3410, 2926, 2875, 1686, 1599, 1265. GC-MS (m/z): 258 [M^+, $C_{15}H_{11}ClO_2$], 260 $[M+2]^+$.

2,5-dihydroxy-3-(4-methoxyphenyl)-2,3-dihydro-1H-inden-1-one (**16a**): ^1H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.92 (dd, *J* = 1.5, 7 Hz, 2H), 7.55-7.52 (m, 2H), 7.07-7.01 (m, 3H), 5.31 (d, *J* = 2 Hz, 1H), 5.22 (d, *J* = 2 Hz, 1H), 4.19 (s, 1H, D_2O exchangeable), 3.91 (s, 3H), 1.61 (s, 1H, D_2O exchangeable). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 195.9, 162.6, 162.2, 136.8, 134.8, 131.4, 129.3, 128.9, 125.6, 116.7, 115.8, 75.4, 63.6, 53.7. IR (KBr, ν_{max} = cm^{-1}): 3408, 2925, 2879, 1685, 1595, 1266, 1089, 858, 731. GC-MS (m/z): 270 [M^+, $C_{16}H_{14}O_4$].

3-(4-bromophenyl)-2,5-dihydroxy-2,3-dihydro-1H-inden-1-one (**18a**): ^1H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.93 (m, 2H), 7.70-7.67 (m, 1H), 7.58-7.53 (m, 2H), 7.08-7.04 (m, 2H), 6.10 (s, 1H, D_2O exchangeable), 5.37 (d, *J* = 2 Hz, 1H), 5.22 (d, *J* = 2.5 Hz, 1H), 4.15 (s, 1H, D_2O exchangeable). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 195.6, 161.9, 137.4, 132.4, 131.9, 131.5, 130.0, 129.8, 126.0, 123.1, 116.3, 75.4, 63.6. IR (KBr, ν_{max} = cm^{-1}): 3433, 2935, 2877, 1687, 1585, 1266, 1088, 862, 733. GC-MS (m/z): 318 [M^+, $C_{15}H_{11}BrO_3$], 320 $[M+2]^+$.

5-chloro-2-hydroxy-3-(4-hydroxyphenyl)-2,3-dihydro-1H-inden-1-one (**20a**): ^1H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.92 (m, 2H), 7.68 (d, *J* = 7.5 Hz, 1H), 7.58-7.50 (m, 2H), 7.43 (d, *J* = 8.5 Hz, 2H), 5.36 (d, *J* = 1.5 Hz, 1H), 5.19 (d, *J* = 2 Hz, 1H), 4.13 (s, 1H, D_2O exchangeable), 1.81 (s, 1H, D_2O exchangeable). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 195.7, 162.4, 161.5, 136.7, 134.7, 131.4, 130.5, 129.4, 128.8, 125.3, 116.2, 75.4, 63.6. IR (KBr, ν_{max} = cm^{-1}): 3417, 2931, 2871, 1681, 1597, 1263, 1081, 860, 737. GC-MS (m/z): 274 [M^+, $C_{15}H_{11}ClO_3$], 276 $[M+2]^+$.

5-bromo-2-hydroxy-3-(4-hydroxyphenyl)-2,3-dihydro-1H-inden-1-one (**21a**): ^1H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.91 (dd, *J* = 1, 8 Hz, 2H), 7.70-7.67 (m, 1H), 7.58-7.54 (m, 2H), 7.43 (t, *J* = 8.5 Hz, 2H), 6.10 (s, 1H, D_2O exchangeable), 5.38 (d, *J* = 2 Hz, 1H), 5.22 (d, *J* = 2.5 Hz, 1H), 4.15 (s, 1H, D_2O exchangeable). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 197.7, 163.9, 161.9, 134.5, 134.2, 133.6, 130.1, 130.0, 129.3, 128.7, 115.7, 76.1, 63.1. IR (KBr, ν_{max} = cm-1): 3427, 2937, 2875, 1685, 1593, 1266, 1083, 864, 727. GC–MS (m/z): 318 [M^+, $C_{15}H_{11}BrO_3$], 320 $[M+2]^+$.

2,6-diphenyltetrahydro-2H-pyran-4-ol (**22a**): ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 7.19-7.41 (m, 8H), 4.51-4.43 (m, 2H), 4.07 (tt, *J* = 4.5, 11.5 Hz, 1H), 2.28 (s, br, D_2O exchangeable, 1H, OH), 2.21 (dd, *J* = 4, 11.5Hz, 2H), 1.53 (q, *J* = 11.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 131.4, 128.3, 127.5, 125.8, 77.8, 68.6, 42.9. IR (KBr, cm^{-1}): 3433, 2965, 2921, 2852, 1634, 1452, 1382, 1265, 1156, 1065, 900, 760, 700. GC-MS (m/z): 410 [M^+, $C_{17}H_{18}O_2$].

2,6-bis(4-chlorophenyl)tetrahydro-2H-pyran-4-ol (**23a**): ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 7.29-7.24 (m, 8H), 4.47 (d, *J* = 11.5 Hz, 2H), 4.06 (tt, *J* = 4.5, 11.5 Hz, 1H), 2.19 (dd, *J* = 4, 11.5 Hz, 2H), 1.48 (q, *J* = 11.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 139.2, 132.3, 127.5, 126.2, 77.8, 67.4, 41.9. IR (KBr, cm^{-1}): 3447, 2960, 2886, 1652, 1543, 1088, 804. GC-MS (m/z): 323 [M^+, $C_{17}H_{16}Cl_2O_2$].

(E)-3-(4-(6-(4-chlorophenyl)-4-hydroxytetrahydro-2H-pyran-2-yl)phenyl)-1-(4-fluorophenyl)prop-2-en-1-one (**24a**): ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 8.18 (d, *J* = 8 Hz, 1H), 7.95 (d, *J* = 8 Hz, 2H), 7.59 (d, *J* = 9 Hz, 3H), 7.48 (d, *J* = 8 Hz, 2H), 7.41 (d, *J* = 9 Hz, 2H), 7.36 (d, *J* = 8.5 Hz, 2H), 7.01 (d, *J* = 9 Hz, 2H), 4.66 (t, *J* = 3 Hz, 2H), 4.14 (tt, *J* = 11, 3 Hz, 1H), 2.22-2.85 (m, 2H), 2.04 (s, br, D_2O exchangeable, 1H), 1.73-1.84 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 188.8, 166.7, 164.6, 144.6, 143.7, 140.8, 134.5, 134.3, 131.2, 130.0, 128.7, 127.7, 126.5, 125.9, 121.6, 115.9, 78.0, 77.7, 69.4, 40.0. IR (KBr, cm^{-1}): 3434, 3010, 2922, 2843, 1734, 1626, 1456, 1256, 1069, 808.8. HRMS (ESIMS): for $C_{26}H_{22}ClFNaO_3$ $(M+Na)^+$ Anal. calcd. 459.1139; found 459.1150.

(E)-1-(4-bromophenyl)-3-(4-(6-(4-bromophenyl)-4-hydroxytetrahydro-2H-pyran-2-yl)phenyl)prop-2-en-1-one (**25a**): ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 7.88 (d, *J* = 8 Hz, 2H), 7.82 (d, *J* = 8.5 Hz, 2H), 7.78 (s, 1H), 7.61-7.66 (m, 4H), 7.47 (s, 1H), 7.35 (d, *J* = 8 Hz, 2H), 7.31-7.32 (m, 2H), 4.45 (d, *J* = 32, 11.5 Hz, 2H), 4.07 (tt, *J* = 10.5, 3 Hz, 1H), 2.30-2.35 (m, 2H), 2.20 (s, br, D_2O exchangeable, 1H), 1.77-1.86 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 189.8, 143.7, 140.7, 135.4, 134.4, 134.1, 129.8, 129.2, 128.5, 128.4, 127.8, 127.5, 126.2, 125.7, 122.0, 77.8, 77.4, 67.2, 39.8. IR (KBr, cm^{-1}): 3454, 2961, 2878, 1651, 1541, 1091, 801. HRMS (ESIMS): for $C_{26}H_{22}Br_2NaO_3$ $(M+Na)^+$ Anal. calcd. 562.9833; found 562.9853.

2-(4-(4-hydroxy-6-phenyltetrahydro-2H-pyran-2-yl)phenyl)-4H-chromen-4-one (**26a**): ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 7.74 (d, *J* = 8 Hz, 2H), 7.37 (dd, *J* = 6, 3 Hz, 2H), 7.27 (d, *J* = 8.5 Hz, 2H), 7.17-7.21 (m, 3H), 7.15 (d, *J* = 8.5 Hz, 2H), 6.92 (s, 1H), 6.79 (dd, *J* = 6.5, 3 Hz, 2H), 4.40 (t, *J* = 11.5 Hz, 2H), 3.90 (tt, *J* = 11, 3 Hz, 1H), 2.15-2.22 (m, 2H), 1.68-1.77 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 190.0, 163.0, 156.0, 139.8, 135.5, 134.1, 131.6, 129.9, 129.3, 128.6, 128.6, 127.6, 127.5, 126.3, 122.2, 121.8, 77.1, 76.9, 65.0, 39.8, 39.7. IR (KBr, cm^{-1}): 3446, 2971, 2880, 1652, 1513, 1208, 799. HRMS (ESIMS): for $C_{26}H_{21}NaO_4$ $(M+Na)^+$ Anal. calcd. 421.1416; found 421.1441.

2-(2-chlorophenyl)-2,3-dihydroquinolin-4(1H)-one (**29a**): ^1H NMR (500 MHz, $CDCl_3$, ppm) δ 11.34 (s, 1H, D_2O exchangeable), 8.58 (d, *J* = 6 Hz, 1H), 7.87 (dd, *J* = 10, 2.5 Hz, 1H), 7.75-7.79 (m, 1H), 7.59 (d, *J* = 10 Hz, 1H), 7.44-7.48 (m, 1H), 7.26-7.29 (m, 1H), 6.98-7.03 (m, 2H), 5.60 (dd, *J* = 13.5, 6.5 Hz, 1H), 3.06-3.16 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 191.2, 160.8, 157.1, 148.4, 138.3, 136.2, 127.1, 123.8, 121.9, 121.4, 121.2, 118.1, 79.1, 42.8. IR (KBr, cm^{-1}): 3164, 2926, 1693, 1606, 1462, 1305, 763. GC-MS (m/z): 257 [M^+, $C_{15}H_{12}ClNO$], 259 $[M+2]^+$.

2-(3,4-dimethoxyphenyl)-2,3-dihydroquinolin-4(1H)-one (**33a**): ^1H NMR (500 MHz, $CDCl_3$, ppm) δ 12.17 (s, 1H, D_2O exchangeable), 7.93 (d, *J* = 10 Hz, 1H), 7.51 (t, *J* = 10.5 Hz, 1H), 7.01-7.08 (m, 4H), 6.91 (d, *J* = 10 Hz, 1H), 5.43 (dd, *J* = 16.5, 2.5 Hz, 1H), 3.93 (s, 3H),

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3.91 (s, 3H), 3.13 (dd, *J* = 21, 17 Hz, 1H), 2.88 (dd, *J* = 21, 2.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 192.2, 161.6, 149.4, 149.3, 136.2, 131.2, 127.1, 120.9, 121.6, 118.8, 118.2, 111.1, 109.4, 79.6, 56.0, 55.9, 44.6. IR (KBr, cm^{-1}): 3110, 2837, 1687, 1598, 1026. GC-MS (m/z): 283 [M+, $C_{17}H_{17}NO_3$].

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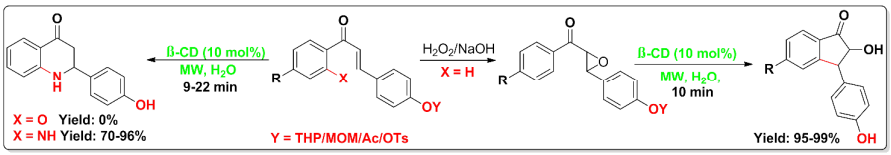

A catalytic method for the deprotection of THP/MOM/Ac/Ts ethers and concomitant cyclization of epoxy chalcone to 2-hydroxyindanone and 2'-aminochalcone to aza-flavanone is reported. This method is "green" and milder but more advanced than those earlier reported.