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Carbonyl Reduction with Zinc

Zinc-Mediated Efficient and Selective Reduction of Carbonyl Compounds

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Abstract: We herein describe for the first time that an optimized combination of Zn and NH_4Cl can be used for the selective reduction of aldehydes and ketones to the corresponding alcohols. The aldehyde and keto groups are selectively reduced in the presence of azide, cyano, epoxy, ester, and carbon–carbon double-bond functional groups. A broad functional-group compatibility, chemoselective reduction of aldehydes in the presence of ketones, and selective reduction of isatins at the C3 carbonyl group are the highlights of the present method.

Introduction

The reduction of aldehydes and ketones is one of the fundamental transformations for the preparation of alcohols, which are used as chemical intermediates for the synthesis of natural products, pharmaceuticals, agrochemicals, and functional materials.[1] Therefore, numerous reduction methods such as metal hydrides,[2] boron-based reagents,[3] catalytic hydrogenation,[4] and biocatalytic reductions[5] have been reported.[1–5] However, many of these methods often generate stoichiometric amounts of waste and involve long reaction times, restricted conditions (under nitrogen; under acidic or alkaline conditions), and complicated operations. Therefore, they pose significant environmental and economic problems, especially in large-scale industrial processes. Furthermore, only a few protocols are known for the chemoselective reduction of aldehydes in the presence of a keto group.[6] In this context, we planned to develop a mild and viable process for the reduction of a wide range of aldehydes, ketones, and isatins in aqueous media.

Aldehydes and ketones undergo pinacol coupling to form the corresponding diols in the presence of excess low-valent metals such as the Zn–Cu couple,[7] Mg,[8] Mn,[9] Zn,[10] Sm,[11] Al,[12] V,[13] and other metals. In these cases, the reduced product is formed as a minor by-product. Recently, it has been reported that Mn in combination with 2,4,6-collidinium hydrochloride can chemoselectively reduce aldehydes to alcohols, while ketones do not react under these conditions.[6c]

Among those metals, Zn has been widely used as a reducing reagent. Zinc in the presence of acetic acid is used as a reducing agent for the reduction of a range of organic functional groups. Zinc amalgam (Zn/Hg alloy) in concentrated HCl is used for the Clemmensen reduction of aldehydes and ketones to provide the corresponding hydrocarbons. Zn is known to reduce benzil and its derivatives to keto-hydroxy compounds.[14] Zn in combination with NH_4Cl has been used for the reduction of nitro and azido groups to the corresponding amines.[15] Zinc is cheap and nontoxic compared to sodium borohydride, a commonly used reagent for the reduction of aldehydes and ketones on a laboratory scale. We envisioned that Zn could be used for the reduction of aldehydes and ketones in the presence of a proton source to selectively obtain the reduced products.

Results and Discussion

We started our optimization studies using 4-methylbenzaldehyde (**1a$_1$**) as a model substrate to optimize the reaction conditions with use of different metals, proton sources at different temperatures, with THF as the solvent (Table 1). The reaction did not proceed by using a catalytic amount of Zn (Table 1, Entry 1). With use of 1 equiv. of Zn, low conversion was observed along with the formation of both the desired alcohol **2a$_1$** and the pinacol product **3a$_1$** (Entries 2 and 3). By increasing the amount of Zn to 3 equiv. as well as increasing the reaction temperature to 60 °C, the formation of **3a$_1$** was decreased but a complete conversion could not be achieved (Entries 4 and 5). To our delight, the reaction proceeded smoothly by using 5 equiv. of Zn leading to the selective formation of **2a$_1$** (Entries 9–10 and 13) even at room temperature. Gratifyingly, 4-methylbenzyl alcohol (**2a$_1$**) was exclusively obtained in just 20 min by using 5 equiv. of Zn in the presence of 8 M aqueous NH_4Cl (10 mL) (Entry 13). When a less concentrated NH_4Cl solution was used, the reaction was slow providing both the alcohol **2a$_1$** and diol **3a$_1$** (Entries 9 and 10). However, a more concentrated NH_4Cl solution did not interfere with the outcome of the reaction. No reaction was observed by using solid NH_4Cl (Entry 11). The use of aqueous NH_4Cl solution (freshly prepared) was necessary as no reaction took place with only H_2O as the proton source (Entry 12). A closely related result was also obtained with HCl (6 N) as the proton source (Entry 17), but the reaction was less efficient than with NH_4Cl (aq.) (Entry 13). The

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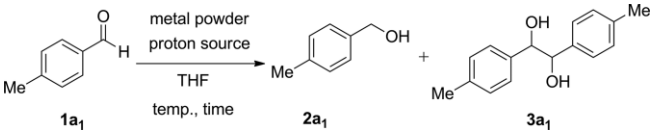
Table 1. Optimization of the reduction of aldehydes.[a]



1a$_1$ **2a$_1$** **3a$_1$**

Entry	Proton source	Metal (equiv.)	*T*	*t*	Conversion [%]; **2a$_1$**/**3a$_1$**[b]
1	NH_4Cl (2 M)	Zn (0.2)	r.t. or 60 °C[c]	6 h	no reaction
2	NH_4Cl (2 M)	Zn (1)	r.t.	4 h	20; 40:60
3	NH_4Cl (2 M)	Zn (1)	60 °C	4 h	25; 50:50
4	NH_4Cl (4 M)	Zn (3)	r.t.	3 h	80; 60:40
5	NH_4Cl (4 M)	Zn (3)	60 °C	3 h	80; 70:30
6	AcOH (4 N)	Zn (3)	r.t. or 60 °C[c]	3 h	90; 60:40
7	HCl (4 N)	Zn (3)	r.t. or 60 °C[c]	3 h	95; 70:30
8	H_2SO_4 (4 N)	Zn (3)	r.t. or 60 °C[c]	3 h	95; 70:30
9	NH_4Cl (4 M)	Zn (5)	r.t.	1 h	100; 90:10
10	NH_4Cl (4 M)	Zn (5)	60 °C	45 min	100; 90:10
11	NH_4Cl[d]	Zn (5)	r.t.	6 h	no reaction
12	H_2O	Zn (5)	r.t.	8 h	no reaction
13	NH_4Cl (8 M)	Zn (5)	r.t.	20 min	100; > 99:1
14	AcOH (4 N)	Zn (5)	r.t. or 60 °C[c]	45 min	100; 90:10
15	HCl (4 N)	Zn (5)	r.t. or 60 °C[c]	1 h	100; 90:10
16	AcOH (6 N)	Zn (5)	r.t. or 60 °C[c]	30 min	100; 95:5
17	HCl (6 N)	Zn (5)	r.t. or 60 °C[c]	30 min	100; 95:5
18	collidine•HCl[e]	Zn (5)	r.t.	20 min	no reaction
19	collidine•HCl[e]	Zn (5)	r.t.	4 h	100; 80:20
20	NH_4Cl (8 M)	Fe (5)	r.t.	20 min	no reaction
21	NH_4Cl (8 M)	Fe (5)	60 °C	20 min	30; 50:50
22	NH_4Cl (8 M)	Mg (5)	r.t. or 60 °C[c]	20 min	70; 70:30
23	NH_4Cl (8 M)	Mn (5)	r.t. or 60 °C[c]	20 min	70; 60:40
24	NH_4Cl (8 M)	In (5)	r.t. or 60 °C[c]	20 min	no reaction

[a] The reactions were performed on a 1.0 mmol scale in THF (2 mL) with use of a proton source (10 mL). [b] The conversion and ratio of **2a$_1$**/**3a$_1$** were determined from crude NMR spectra of the reaction mixture. [c] The outcome of the reaction remained similar at 60 °C. [d] With use of solid NH_4Cl (5 equiv.). [e] With use of collidine•HCl (5 equiv.).

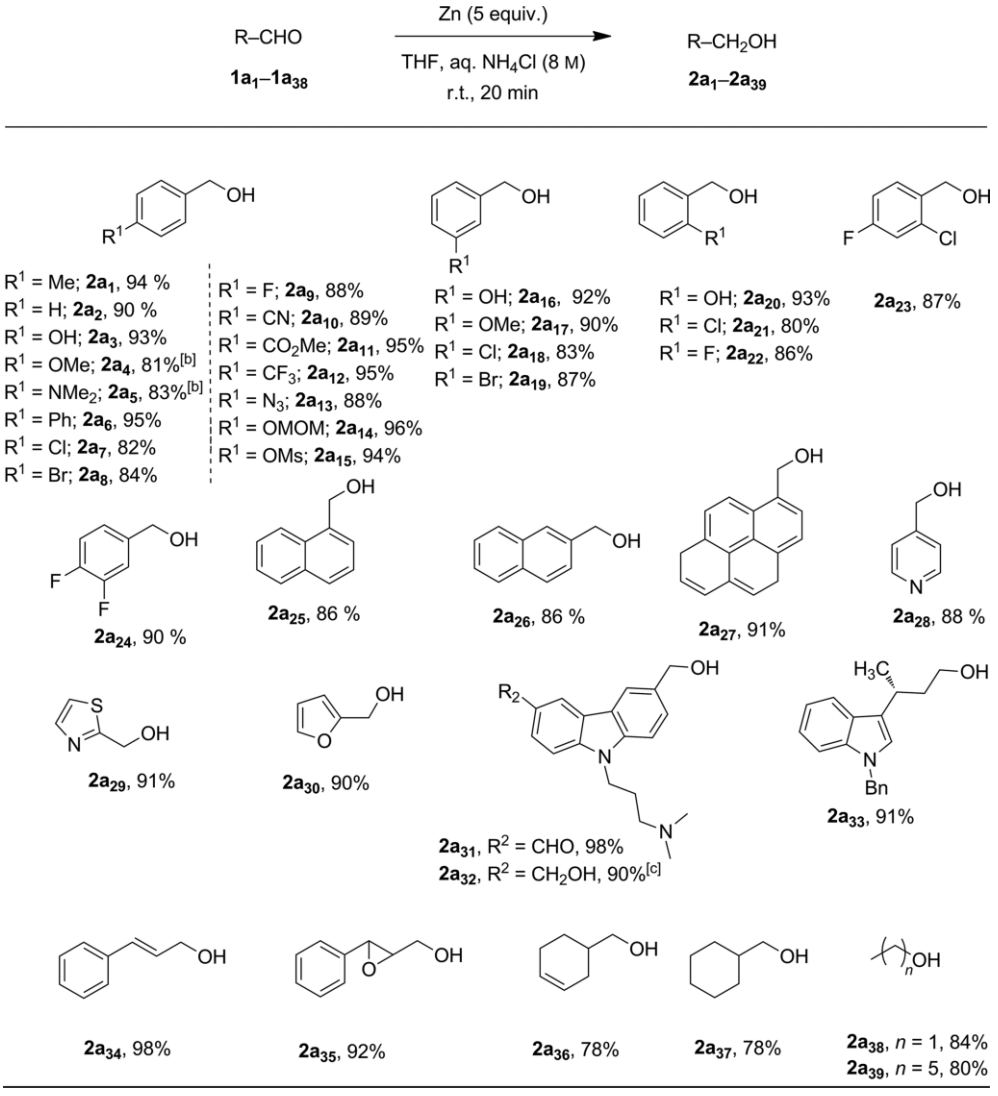
reaction also proceeded in the presence of AcOH (6 N), but a trace amount of diol **3a$_1$** was also formed (Entry 16). When the reaction was performed with use of 5 equiv. of collidine•HCl as a proton source,[6c] no product was formed after 20 min at room temperature (Entry 18). However, a complete conversion of **1a$_1$** was observed with a longer reaction time (4 h at room temperature), providing alcohol **2a$_1$** as the major product along with pinacol **3a$_1$** (Entry 19). The reduction of **1a$_1$** in deuterated solvents such as [D_8]THF and D_2O suggests that NH_4Cl (aq.) is the proton source (see the Supporting Information, Table S1).

It is worth mentioning that Zn and aqueous NH_4Cl solution were added at the same time to make the reaction faster by preventing the formation of the pinacol product. The other metal sources such as Fe, Mn, Mg, and In were inefficient (Table 1, Entries 20–24). The reaction with Mg and Mn provided both the reduced and the pinacol products (Table 1, Entries 22 and 23). Then, various solvents including DMF, DMSO, MeCN, CH_2Cl_2, H_2O, toluene, and dioxane were evaluated (Entries 1–9 in Table S2, Supporting Information). The solvent screening results showed that the highest yield of **2a$_1$** (95 %) was obtained when THF was used as the solvent (Table S2, Supporting Information). The reaction also proceeded in dioxane, toluene, and CH_3CN; but a poor conversion was observed with the use of DMSO, DMF, CH_2Cl_2, and DCE (Table S2, Supporting Information). No reaction took place by using only water as the solvent (Table S2, Supporting Information). We determined the optimal reaction conditions to selectively obtain the reduced product **2a$_1$** as follows: Zn (5 equiv.), 8 M NH_4Cl (10 mL) in THF (2 mL), room temp., 20 min.

With the optimal reaction conditions in hand, we explored the substrate scope of the Zn-mediated reduction of aldehydes (Table 2). We found that a wide range of aldehydes irrespective of the substituent position and electronic properties were smoothly reduced to give the corresponding alcohols in good to excellent yields. The reduction of *p*-anisaldehyde and 4-(dimethylamino)benzaldehyde proceeded slowly at room temperature, but they were efficiently reduced upon heating at 60 °C for 3 h to provide benzyl alcohols **2a$_4$** (81 %) and **2a$_5$** (83 %), respectively, in high yields; some amount of the pinacols (15 and 12 %, respectively) was also obtained. Many functional groups such as OH, Cl, Br, F, CN, CO_2Me (**2a$_3$**, **2a$_7$**–**a$_{11}$**) were tolerated. Importantly, the aldehyde group was selectively reduced in the presence of an azido (**2a$_{13}$**) and an epoxy group (**2a$_{35}$**). The labile methoxymethyl (MOM) and mesyl (Ms) groups were well tolerated under the reaction conditions (**2a$_{14}$**, **2a$_{15}$**).

Polycyclic aromatic aldehydes and heterocyclic aldehydes also furnished the corresponding benzyl alcohols (**2a$_{25}$**–**a$_{27}$**, **2a$_{28}$**–**a$_{33}$**) in excellent yields. The carbazoledialdehyde[16] gave the reduced monoaldehyde derivative **2a$_{31}$** in excellent yield at room temperature after 20 min. However, both the formyl groups were reduced by conducting the reaction for 45 min to provide diol **2a$_{32}$** in excellent yield. In the cases of pyridine-4-

Table 2. Reduction of aldehydes.[a]



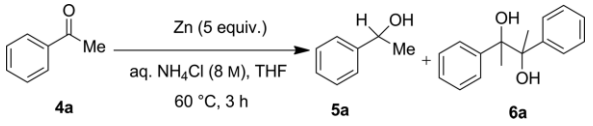
[a] The reactions were performed on a 1.0 mmol scale with use of Zn (5 equiv.), THF (2 mL), 8 M NH_4Cl (aq.) solution (10 mL) at room temp. for 20 min. [b] 60 °C for 3 h; 15 and 12 % of pinacols isolated. [c] The reaction was carried out at room temp. for 45 min.

carbaldehyde and 4-cyanobenzaldehyde, trace amounts of the corresponding pinacols were also formed, but the reduced products were easily separated by column chromatography (**2a$_{28}$** and **2a$_{10}$**). In all the other cases, no column chromatographic purification was needed as the corresponding alcohols were obtained in nearly quantitative yields. Interestingly, the chiral indolyl aldehyde[17] underwent facile reduction to give the corresponding alcohol **2a$_{33}$** with retention of the stereochemistry. The α,β-unsaturated aldehyde gave the desired alcohol **2a$_{34}$**,[6g,6i] in which the (*E*) stereochemistry was preserved. Aliphatic aldehydes provided their corresponding alcohols in excellent yields at room temperature, but these reactions took a slightly longer time with formation of trace amounts of the pinacol products (**2a$_{36}$**–**a$_{39}$**). Pivalaldehyde and cyclopropanecarbaldehyde did not furnish the desired products under the optimized reaction conditions. Since excess Zn was used in the reduction, we recovered the used Zn after completion of the reaction and reused it to carry out further reactions. Zn showed diminished activity in subsequent reaction cycles (Table S3, Supporting Information).

We were delighted to find out that ketones, although they reacted slowly under the optimized reaction conditions, gave the desired alcohols **5** as the major products at 60 °C (Table 3). The reduction of ketone **4a** was inefficient with use of collidinium hydrochloride (Entries 6 and 7);[6c] a low (40 %) conversion of **4a** occurred after 3 h at 60 °C, and a mixture of alcohol **5a** and diol **6a** was obtained by performing the reaction for a longer time (8 h).

Aromatic ketones containing OH, OMe, NH_2, and Br groups were efficiently reduced to produce the corresponding secondary alcohols (**5c**–**f**). Importantly, the keto group was reduced selectively in the presence of esters, double bonds, and epoxy groups (**5n**,**k**,**l**). The 2,2,2-trifluoroacetophenone derivative **4g** was reduced to afford the corresponding fluorinated secondary alcohol **5g** in high yield. It is important to note that benzophenone (**4h**) gave exclusively alcohol **5h** in excellent yield

Table 3. Optimization of the reduction of ketones.[a]

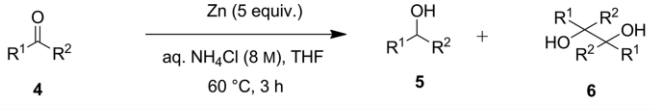


4a 5a 6a

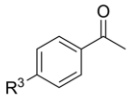
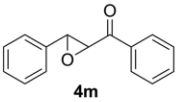
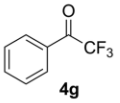
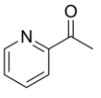
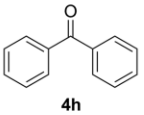
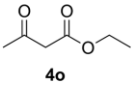
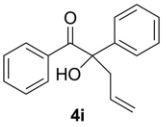
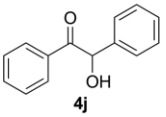
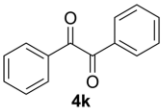
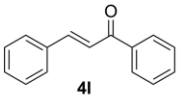
Entry	Zn [equiv.]	*T* [°C]	*t* [h]	Conversion [%]; ratio of **5a**/**6a**[b]	**6a** (*dl*/*meso*)[c]
1	3	r.t.	6	10; 50:50	n.d.
2	3	60	6	70; 60:40	50:50
3	5	r.t.	4	40; 60:40	n.d.
4	5	60	3	100; 75:25	60:40
5	5	r.t.	14	80; 50:50	n.d.
6	5	60	3	40; 60:40[d]	n.d.
7	5	60	8	>99; 50:50[d]	n.d.

[a] The reactions were performed on a 1.0 mmol scale in solvent (2 mL). [b] Conversion and ratio (**5a**/**6a**) were determined from NMR spectra of the crude reaction mixture; n.d.: not determined. [c] The *dl*/*meso* ratio was determined from the NMR spectra of isolated **6a**. [d] The reactions were performed with collidinium hydrochloride (5 equiv.).

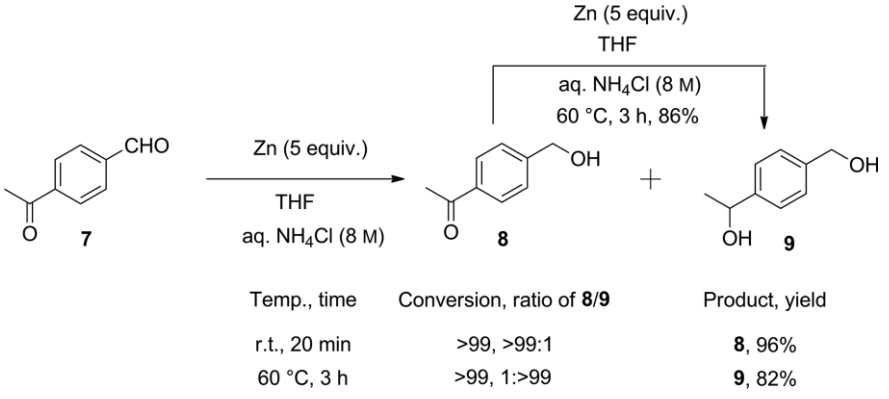
Table 4. Reduction of ketones.[a]



4 5 6

Substrate	Product	Substrate	Product
 R^3 = H (**4a**), Me (**4b**), Br (**4c**), OH (**4d**), OMe (**4e**), NH_2 (**4f**)	**5a**, 75%; **6a** (25%, 55:45)[b] **5b**, 73%; **6b** (27%, 60:40)[b] **5c**, 82%; **6c**[c] **5d**, 77%; **6d**[c] **5e**, 74%[c] **5f**, 80%[c]	 **4m**	**5l**, 88%[d]
 **4g**	**5g**, 84%[c]	 **4n**	**5m**, 80%[c,e]
 **4h**	**5h**, 92%[d]	 **4o**	**5n**, 78%[c]
 **4i**	**5i**, 80% (>99:1 *syn*/*anti*)[b,d]	 **4p**	**5o**, 74%[c,e]
 **4j**	**5j**, 86% (90:10)[d]	 **4q**	**5p**, 74%[c,e]
 **4k**	**5j**, 82% (90:10)[d]	 **4r**	**5q**, 72%[c,e]
 **4l**	**5k**, 86%[d]		

[a] The reactions were performed on a 1.0 mmol scale with use of Zn (5 equiv.), THF (2 mL), 8 M NH_4Cl (aq.) solution (10 mL) at 60 °C for 3 h. [b] The *dl*/*meso* and *syn*/*anti* ratios were determined from the NMR spectra of the isolated pinacol products. [c] The pinacol product was not isolated. [d] The pinacol product was not formed. [e] Reaction time: 4 h.



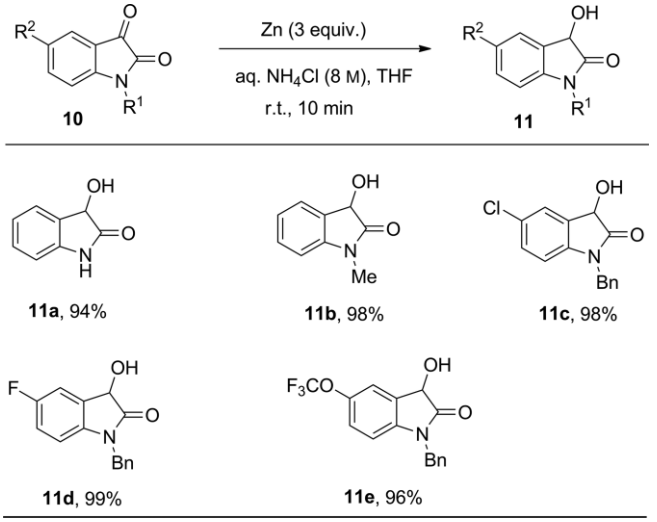
Scheme 1. Chemoselective reduction of an aldehyde in the presence of a ketone.

(92 %), better than the reported metal-mediated reductions.[8,9] The α-keto-hydroxy derivatives **4i** and **4j** were reduced efficiently to give the desired products **5i** (*syn*/*anti* > 99:1) and **5j** (*dl*/*meso* = 90:10), respectively, in excellent yields and diastereoselectivities. Both keto groups of benzil (**4k**) were reduced to provide diol **5j** (*dl*/*meso* = 90:10). Heteroaryl (**4n**), cyclic (**4p**–**q**), and acyclic (**4r**) aliphatic ketones were also reduced to give the corresponding reduced products within a slightly longer reaction time (4 h). In a few cases, the pinacol products **6** were obtained as the minor products (0–27 %), which could be easily separated by column chromatography (Table 4).

Next, we evaluated the chemoselectivity of the reduction process by using 4-acetylbenzaldehyde (**7**) (Scheme 1) as the substrate. At room temperature, benzyl alcohol **8** was isolated as the sole product in 90 % yield, indicating that the reduction of aldehydes could be performed with excellent selectivity without concomitant reduction of the keto group. Many reducing agents would have reacted with both functional groups providing a mixture of products.[1–5] Although a few methods have been developed for the chemoselective reduction of aldehydes in the presence of ketones,[6] the development of a practical and bench-scale process is still desirable. We have established a mild protocol for the chemoselective reduction of aldehydes in the presence of ketones that can be applied for large-scale synthesis. By heating aldehyde **7** at 60 °C for 3 h, both aldehyde and keto groups were reduced to provide diol **9**, which was also obtained from the hydrogenation of **8**.

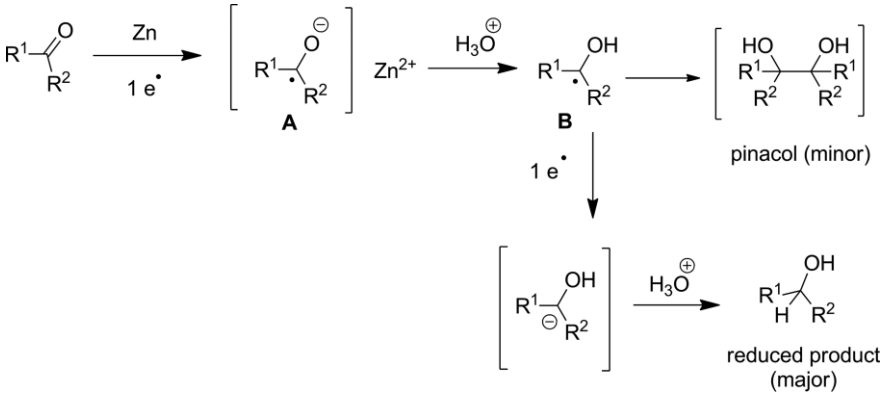
The method was also used to achieve the selective reduction of the C3 carbonyl group of isatins (Table 5). Only a few methods are known for the reduction of isatins.[18] $NaBH_4$ is the commonly used reagent for the selective reduction of isatin derivatives at the C3 position; however, 5-halo-substituted isatins gave the corresponding 3-hydroxyindolines in poor yields. Recently, a combination of $CeCl_3$ and $NaBH_4$ has been developed for the efficient reduction of 5-halo-substituted isatins.[19] In contrary, our reaction conditions (3 equiv. Zn, aqueous 8 M NH_4Cl in THF) constitute a mild and simple alternative for the chemoselective reduction of isatins, affording the 3-hydroxyindoline derivatives **11** in nearly quantitative yields. The 5-halo-substituted isatins were reduced efficiently under the optimized reaction conditions, affording the corresponding 3-hydroxyindolines in excellent yields without any column chromatographic purification. The reactions were completed within 10 min. Moreover, these reductions could be easily performed on a gram scale; the reductions of 4-methylbenzaldehyde and *N*-methylisatin were carried out on a 2 g scale to provide the corresponding reduced products in 90 and 94 % yields, respectively.

Table 5. Reduction of isatin derivatives.[a]



[a] The reactions were performed on a 1.0 mmol scale with use of Zn (3 equiv.), THF (2 mL), 8 M NH_4Cl (aq.) (10 mL) at room temp. for 10 min.

The reduction process proceeds through a typical single electron-transfer (SET) mechanism. The reduction of $\mathbf{1a_1}$ was inhibited in the presence of radical scavengers such as TEMPO or galvinoxyl, corroborating a radical pathway (Table S4, Supporting Information). The electron transfer from Zn to the aldehyde and ketone functional groups generates a reactive alkoxy radical intermediate **A**, which upon protonation in the presence of aqueous NH_4Cl forms the radical intermediate **B** (Scheme 2). The intermediate **B** can undergo radical coupling to form the pinacol, or it can follow another electron transfer to form the reduced alcohol. Since the pinacol product is obtained as a minor product, the electron transfer and subsequent protonation are faster than the radical coupling to provide the reduced alcohol as the major product.



Scheme 2. Proposed mechanism through a SET pathway.

Conclusions

We have developed a general protocol for the reduction of different kinds of aldehydes (aliphatic, aromatic, polycyclic aromatic, heterocyclic, and α,β-unsaturated) and ketones to the corresponding alcohols using an optimized amount of Zn and NH_4Cl under mild reaction conditions. The method can be used for the rapid reduction of isatins at the C3 position. The reactions proceed efficiently with excellent yields and high chemoselectivity. In most cases, the products were isolated directly without chromatographic purification. The selective reduction of the aldehyde group is achieved in the presence of ketones, ester, cyano, azide, and epoxy groups and carbon–carbon double bonds, thus providing a mild, economic, and attractive alternative to other reagents.

Experimental Section

General Information: All experiments were carried out under open atmosphere in flame-dried flasks. Solvents were dried by using standard procedures. All starting materials were obtained from commercial suppliers and used as received. Products were purified by flash chromatography on silica gel (100–200 mesh, Merck). Unless otherwise stated, yields refer to analytically pure samples. NMR spectra were recorded in $CDCl_3$ and [D_6]DMSO. ^1H NMR spectra were recorded with 500 MHz and 400 MHz instruments at 278 K. Data is reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants [Hz], and integration. ^{13}C NMR spectra were recorded at either 100 MHz or at 125 MHz with complete proton decoupling. Chemical shifts (δ) are reported in ppm.

General Procedure for the Reduction of Aldehydes (GP-I): To a solution of aldehydes **1** (1.0 mmol, 1 equiv.) in THF (2 mL) were added Zn dust (5 mmol, 325 mg, 5 equiv.) and aqueous NH_4Cl solution (8 M, 10 mL) simultaneously. The reaction mixture was stirred at room temperature until complete conversion of starting material (as monitored by TLC), typically for 20 min. The reaction mixture was filtered through cotton into a separatory funnel and extracted with EtOAc (3 × 5 mL). The combined organic extracts were washed with brine, dried with anhydrous Na_2SO_4, filtered, and the solvent was evaporated to give the corresponding alcohols **2**. In most cases, the product was sufficiently pure, and no further purification was needed.

General Procedure for the Reduction of Ketones (GP-II): To a solution of ketones **4** (1 mmol, 1 equiv.) in THF (2 mL) were added Zn dust (5 mmol, 325 mg, 5 equiv.) and aqueous NH_4Cl solution (8 M, 10 mL) simultaneously. The reaction mixture was stirred at 60 °C until complete conversion of starting material (as monitored by TLC), typically for 3–4 h. The reaction mixture was filtered through cotton into a separatory funnel and extracted with EtOAc (3 × 5 mL). The combined organic extracts were washed with brine, dried with anhydrous Na_2SO_4, filtered, and the solvent was evaporated. The residue was purified by column chromatography on silica gel by using hexanes/EtOAc as eluent (80:20 to 60:40) to give the corresponding secondary alcohols **5**. In some cases, the pinacol product **6** was obtained as a minor product, which was separated by using column chromatography.

General Procedure for Reduction of Isatins (GP-III): To a solution of isatins **10** (1 mmol, 1 equiv.) in THF (2 mL) were added Zn dust (3 mmol, 195 mg, 3 equiv.) and aqueous NH_4Cl solution (8 M, 10 mL) simultaneously. The reaction mixture was stirred at room temperature until complete conversion of the starting material (as monitored by TLC), typically for 10 min. The reaction mixture was filtered through cotton into a separatory funnel and extracted with EtOAc (3 × 5 mL). The combined organic extracts were washed with brine, dried with anhydrous Na_2SO_4, filtered, and the solvent was evaporated to give the desired products **11**. The product thus obtained was sufficiently pure, and no further purification was needed.

Gram-Scale Experiments

Preparation of 4-Methylbenzyl Alcohol ($2a_1$): To a solution of 4-methylbenzaldehyde ($1a_1$) (2.0 g, 16.6 mmol, 1.0 equiv.) in THF (20 mL) were added Zn dust (5.4 g, 83 mmol, 5.0 equiv.) and aqueous NH_4Cl solution (8 M, 40 mL) simultaneously. The reaction mixture was stirred at room temperature until completion of the reaction (as monitored by TLC); for 30 min to be specific in this case. The reaction mixture was filtered through cotton into a separatory funnel and extracted with EtOAc (3 × 20 mL). The combined organic extracts were washed with brine, dried with anhydrous Na_2SO_4, filtered, and the solvent was evaporated to give $2a_1$ (1.8 g, 92 %) as a colorless liquid.

Preparation of 3-Hydroxy-1-methylindolin-2-one (11b): To a solution of *N*-methylisatin (**10b**) (2.0 g, 12.4 mmol, 1.0 equiv.) in THF (15 mL) were added Zn dust (2.5 g, 38.0 mmol, 3 equiv.) and aqueous NH_4Cl solution (8 M, 40 mL) simultaneously. The reaction mixture was stirred at room temperature until completion of the reaction (as monitored by TLC); for 15 min to be specific in this case. The reaction mixture was filtered through cotton into a separatory

funnel and extracted with EtOAc (3 × 20 mL). The combined organic extracts were washed with brine, dried with anhydrous Na_2SO_4, filtered, and the solvent was evaporated to give **11b** (1.94 g, 95 %) as a pale yellow solid.

Analytic Data of the Compounds

4-Methylbenzyl Alcohol (2a$_1$):[6f] According to GP-I, 4-methylbenzaldehyde (**1a$_1$**) (120 mg, 1.0 mmol, 1.0 equiv.) afforded **2a$_1$** (114 mg, 94 %) as a colorless liquid. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 2.10 (s, 3 H), 4.30 (s, 2 H), 4.96 (br. s, 1 H), 6.94 (d, J = 8.2 Hz, 2 H), 7.04 (d, J = 8.2 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 20.8, 62.9, 126.6, 128.7, 135.7, 139.6 ppm. HRMS (ESI): calcd. for $C_8H_{10}O$ [M + H]$^+$ 123.0732; found 123.0735.

Benzyl Alcohol (2a$_2$):[6f] According to GP-I, benzaldehyde (**1a$_2$**) (106 mg, 1.0 mmol, 1.0 equiv.) afforded **2a$_2$** (98 mg, 90 %) as a colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.90 (br. s, 1 H), 4.65 (s, 2 H), 7.23–7.35 (m, 5 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 65.1, 127.0, 127.5, 128.5, 140.9 ppm. HRMS (ESI): calcd. for C_7H_8O [M + H]$^+$ 109.0575; found 109.0572.

4-Hydroxybenzyl Alcohol (2a$_3$):[20] According to GP-I, 4-hydroxybenzaldehyde (**1a$_3$**) (122 mg, 1.0 mmol, 1.0 equiv.) afforded **2a$_3$** (116 mg, 93 %) as a colorless liquid. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 4.37 (s, 2 H), 4.90 (br. s, 1 H), 6.72 (d, J = 8.4 Hz, 2 H), 7.0 (d, J = 8.4 Hz, 2 H), 9.23 (s, 1 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 62.9, 114.8, 128.1, 132.8, 156.2 ppm. HRMS (ESI): calcd. for $C_7H_8O_2$ [M + H]$^+$ 125.0524; found 125.0522.

(4-Methoxyphenyl)methanol (2a$_4$):[6f] According to GP-II, 4-methoxybenzaldehyde (**1a$_4$**) (136 mg, 1.0 mmol, 1.0 equiv.) afforded **2a$_4$** (112 mg, 81 %) as a colorless liquid. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 3.61 (s, 3 H), 4.31 (d, J = 6.7 Hz, 2 H), 4.94 (t, J = 6.7 Hz, 1 H), 6.76 (d, J = 11.0 Hz, 2 H), 7.12 (d, J = 11.0 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 54.9, 62.6, 113.5, 127.9, 134.6, 158.2 ppm. HRMS (ESI): calcd. for $C_8H_{10}O_2$ [M + H]$^+$ 139.0681; found 139.0680.

[4-(Dimethylamino)phenyl]methanol (2a$_5$):[6j] According to GP-II, 4-(dimethylamino)benzaldehyde (**1a$_5$**) (148 mg, 1.0 mmol, 1.0 equiv.) afforded **2a$_5$** (126 mg, 83 %) as a straw-yellow liquid. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 2.88 (s, 6 H), 4.39 (d, J = 5.7 Hz, 2 H), 4.96 (t, J = 5.65 Hz, 1 H), 6.71 (d, J = 8.8 Hz, 2 H), 7.16 (d, J = 8.8 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 40.4, 63.0, 112.3, 127.9, 130.2, 149.7 ppm. HRMS (ESI): calcd. for $C_9H_{13}NO$ [M + H]$^+$ 152.0997; found 152.0999.

1,1′-Biphenyl-4-ylmethanol (2a$_6$):[6g] According to GP-I, 1,1′-biphenyl-4-carbaldehyde (**1a$_6$**) (182 mg, 1.0 mmol, 1.0 equiv.) afforded **2a$_6$** (87 mg, 95 %) as a colorless liquid. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 4.57 (d, J = 5.7 Hz, 2 H), 5.30 (t, J = 5.7 Hz, 1 H), 7.34 (t, J = 7.6 Hz, 1 H), 7.46–7.41 (m, 4 H), 7.65–7.60 (m, 4 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 62.7, 126.4, 126.6, 127.1, 127.3, 128.9, 138.7, 140.2, 141.8 ppm. HRMS (ESI): calcd. for $C_{13}H_{12}O$ [M + H]$^+$ 185.0888; found 185.0889.

4-Chlorobenzyl Alcohol (2a$_7$):[6b] According to GP-I, 4-chlorobenzaldehyde (**1a$_7$**) (140 mg, 1.0 mmol, 1.0 equiv.) afforded **2a$_7$** (116 mg, 82 %) as a straw-yellow liquid. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 4.35 (d, J = 5.6 Hz, 2 H), 5.17 (t, J = 6.4 Hz, 1 H), 7.15 (d, J = 8.2 Hz, 2 H), 7.48 (d, J = 8.8 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 62.1, 119.5, 128.5, 130.8, 141.8 ppm. HRMS (ESI): calcd. for C_7H_7ClO [M + H]$^+$ 143.0185; found 143.0183.

4-Bromobenzyl Alcohol (2a$_8$):[6h] According to GP-I, 4-bromobenzaldehyde (**1a$_8$**) (184 mg, 1.0 mmol, 1.0 equiv.) afforded **2a$_8$** (158 mg, 84 %) as a straw-yellow liquid. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 4.45 (d, J = 5.7 Hz, 2 H), 5.27 (t, J = 6.3 Hz, 1 H), 7.25 (d, J = 8.2 Hz, 2 H), 7.48 (d, J = 8.8 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 62.2, 119.6, 128.6, 130.9, 141.9 ppm. HRMS (ESI): calcd. for C_7H_7BrO [M + H]$^+$ 186.9680; found 186.9678.

4-Fluorobenzyl Alcohol (2a$_9$):[6g] According to GP-I, 4-fluorobenzaldehyde (**1a$_9$**) (124 mg, 1.0 mmol, 1.0 equiv.) afforded **2a$_9$** (110 mg, 88 %) as a colorless liquid. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 4.37 (d, J = 5.6 Hz, 2 H), 5.13 (t, J = 5.6 Hz, 1 H), 7.0–7.10 (m, 2 H), 7.24 (dd, J = 6.3, 2.5 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 62.2, 114.6, 114.8, 128.3, 128.4, 138.6, 138.7, 160.2, 162.1 ppm. HRMS (ESI): calcd. for C_7H_7FO [M + H]$^+$ 127.0481; found 127.0479.

4-Cyanobenzyl Alcohol (2a$_{10}$):[6h] According to GP-I, 4-cyanobenzaldehyde (**1a$_{10}$**) (130 mg, 1.0 mmol, 1.0 equiv.) afforded **2a$_{10}$** (118 mg, 89 %) as a colorless liquid. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 4.52 (d, J = 5.0 Hz, 2 H), 5.38 (t, J = 5.9 Hz, 1 H), 7.44 (d, J = 7.5 Hz, 2 H), 7.71 (d, J = 7.5 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 62.2, 109.3, 119.0, 126.9, 132.0, 148.5 ppm. HRMS (ESI): calcd. for C_8H_7NO [M + H]$^+$ 134.0528; found 134.0526.

Methyl 4-(Hydroxymethyl)benzoate (2a$_{11}$):[6f] According to GP-I, methyl 4-formylbenzoate (**1a$_{11}$**) (164 mg, 1.0 mmol, 1.0 equiv.) afforded **2a$_{11}$** (158 mg, 95 %). ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 3.80 (s, 3 H), 4.53 (d, J = 7.4 Hz, 2 H), 5.30 (t, J = 7.7 Hz, 1 H), 7.42 (d, J = 9.8 Hz, 2 H), 7.88 (d, J = 9.8 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 51.9, 62.4, 126.2, 126.3, 129.0, 148.3, 166.2 ppm. HRMS (ESI): calcd. for $C_9H_{10}O_3$ [M + H]$^+$ 167.0630; found 167.06329.

[4-(Trifluoromethyl)phenyl]methanol (2a$_{12}$):[6h] According to GP-I, 4-trifluoromethylbenzaldehyde (**1a$_{12}$**) (174 mg, 1.0 mmol, 1.0 equiv.) afforded **2a$_{12}$** (168 mg, 95 %). ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 4.62 (d, J = 5.0 Hz, 2 H), 5.48 (t, J = 5.7 Hz, 1 H), 7.55 (d, J = 8.2 Hz, 2 H), 7.68 (d, J = 8.2 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 62.3,123.1, 124.9, 125.9, 126.9, 127.3, 127.7, 147.5 ppm. HRMS (ESI): calcd. for $C_8H_7F_3O$ [M + H]$^+$ 177.0449; found 177.0449.

(4-Azidophenyl)methanol (2a$_{13}$):[21] According to GP-I, 4-azidobenzaldehyde (**1a$_{13}$**) (146 mg, 1.0 mmol, 1.0 equiv.) afforded **2a$_{13}$** (134 mg, 90 %) as a straw-yellow solid. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 4.47 (d, J = 5.9 Hz, 2 H), 5.22 (t, J = 5.9 Hz, 1 H), 7.06 (d, J = 8.3 Hz, 2 H), 7.25 (d, J = 8.3 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 62.3, 118.7, 128.1, 137.6, 139.6 ppm. HRMS (ESI): calcd. for $C_7H_7N_3O$ [M + H]$^+$ 150.0589; found 150.0588.

[4-(Methoxymethoxy)phenyl]methanol (2a$_{14}$): According to GP-I, 4-(methoxymethoxy)benzaldehyde (**1a$_{14}$**) (166 mg, 1.0 mmol, 1.0 equiv.) afforded **2a$_{14}$** (164 mg, 96 %) as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.46 (s, 3 H), 4.56 (s, 2 H), 5.15 (s, 2 H), 7.00 (d, J = 8.8 Hz, 2 H), 7.25 (d, J = 8.3 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.9, 64.6, 94.5, 116.7, 128.5, 134.7, 156.7 ppm. HRMS (ESI): calcd. for $C_9H_{12}O_3$ [M + H]$^+$ 169.0786; found 169.0784.

4-(Hydroxymethyl)phenyl Methanesulfonate (2a$_{15}$): According to GP-I, 4-formylphenyl methanesulfonate (**1a$_{15}$**) (200 mg, 1.0 mmol, 1.0 equiv.) afforded **2a$_{15}$** (190 mg, 94 %) as a pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.12 (s, 3 H), 4.65 (s, 2 H), 7.27–7.23 (m, 2 H), 7.41–7.36 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 37.4, 64.2, 122.1, 128.5, 140.4, 148.5 ppm. HRMS (ESI): calcd. for $C_8H_{10}O_4S$ [M + H]$^+$ 203.0300; found 203.0301.

3-Hydroxybenzyl Alcohol (2a$_{16}$):[20] According to GP-I, 3-hydroxybenzaldehyde (**1a$_{16}$**) (122 mg, 1.0 mmol, 1.0 equiv.) afforded **2a$_{16}$** (114 mg, 92 %) as a colorless liquid. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 4.42 (d, J = 5.1 Hz, 2 H), 5.10 (t, J = 5.7 Hz, 1 H), 6.62 (dd, J = 1.9, 5.7 Hz, 1 H), 6.72 (d, J = 7.6 Hz, 1 H), 6.76 (s, 1 H), 7.10 (t, J = 8.0 Hz, 1 H), 9.27 (s, 1 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ =

63.0, 113.4, 113.6, 117.1, 129.1, 144.1, 157.3 ppm. HRMS (ESI): calcd. for $C_7H_8O_2$ $[M + H]^+$ 125.0524; found 125.0524.

(3-Methoxyphenyl)methanol ($2a_{17}$):[6f] According to GP-I, 3-methoxybenzaldehyde (**$1a_{17}$**) (136 mg, 1.0 mmol, 1.0 equiv.) afforded **$2a_{17}$** (124 mg, 90 %) as a colorless liquid. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 3.72 (3 H, d, J = 2.0 Hz), 4.48 (d, J = 5.5 Hz, 2 H), 5.19 (t, J = 6.1 Hz, 1 H), 6.76 (d, J = 10.3 Hz, 1 H), 6.90 (s, 2 H), 7.21 (t, J = 7.3 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 54.9, 62.8, 111.8, 112.1, 118.5, 129.1, 144.3, 159.3 ppm. HRMS (ESI): calcd. for $C_8H_{10}O_2$ $[M + H]^+$ 139.0681; found 139.0680.

3-Chlorobenzyl Alcohol ($2a_{18}$):[6b] According to GP-I, 3-chlorobenzaldehyde (**$1a_{18}$**)(140 mg, 1.0 mmol, 1.0 equiv.) afforded **$2a_{18}$** (118 mg, 83 %) as a straw-yellow liquid. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 4.50 (d, J = 1.9 Hz, 2 H), 5.40–5.35 (m, 1 H), 7.24 (d, J = 7.6 Hz, 2 H), 7.33–7.30 (m, 1 H), 7.35 (s, 1 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 62.3, 125.0, 126.2, 126.6, 130.0, 133.0, 145.3 ppm. HRMS (ESI): calcd. for C_7H_7ClO $[M + H]^+$ 143.0185; found 143.0183.

3-Bromobenzyl Alcohol ($2a_{19}$):[6f] According to GP-I, 3-bromobenzaldehyde (**$1a_{19}$**) (184 mg, 1.0 mmol, 1.0 equiv.) afforded **$2a_{19}$** (162 mg, 87 %) as a straw-yellow liquid. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 4.51 (d, J = 5.7 Hz, 2 H), 5.38 (t, J = 5.7 Hz, 1 H), 7.32–7.36 (m, 2 H), 7.41 (d, J = 7.6 Hz, 1 H), 7.52 (s, 1 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 62.2, 121.6, 125.3, 129.1, 129.5, 130.3, 145.5 ppm. HRMS (ESI): calcd. for C_7H_7BrO $[M + H]^+$ 186.9680; found 186.9678.

2-Hydroxybenzyl Alcohol ($2a_{20}$):[6k] According to GP-I, 2-hydroxybenzaldehyde (**$1a_{20}$**) (122 mg, 1.0 mmol, 1.0 equiv.) afforded **$2a_{20}$** (116 mg, 93 %) as a colorless liquid. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 4.45 (s, 2 H), 4.93 (br. s, 1 H), 6.79 (t, J = 10.8 Hz, 2 H), 7.02–7.05 (m, 1 H), 7.28 (d, J = 6.7 Hz, 1 H), 9.28 (s, 1 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 58.3, 114.5, 118.6, 127.2, 127.3, 128.5, 154.1 ppm. HRMS (ESI): calcd. for $C_7H_8O_2$ $[M + H]^+$ 125.0524; found 125.0523.

2-Chlorobenzyl Alcohol ($2a_{21}$):[6b] According to GP-I, 2-chlorobenzaldehyde (**$1a_{21}$**) (140 mg, 1.0 mmol, 1.0 equiv.) afforded **$2a_{21}$**(114 mg, 80 %) as a straw-yellow liquid. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 4.50 (d, J = 5.65 Hz, 2 H), 5.35 (t, J = 5.65 Hz, 1 H), 7.16–7.12 (m, 1 H), 7.26–7.21 (m, 2 H), 7.47 (d, J = 7.55 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 60.5, 127.1, 128.2, 128.3, 128.8, 131.2, 139.6 ppm. HRMS (ESI): calcd. for C_7H_7ClO $[M + H]^+$ 143.0185; found 143.0183.

2-Fluorobenzyl Alcohol ($2a_{22}$):[6g] According to GP-I, 2-fluorobenzaldehyde (**$1a_{22}$**) (124 mg, 1.0 mmol, 1.0 equiv.) afforded **$2a_{22}$** (108 mg, 86 %) as a colorless liquid. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 4.55 (d, J = 5.7 Hz, 2 H), 5.32–5.29 (m, 1 H), 7.13–7.09 (m, 1 H), 7.18–7.15 (m, 1 H), 7.30–7.26 (m, 1 H), 7.48–7.45 (m, 1 H) ppm. ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 56.7, 56.8, 114.7, 114.9, 124.2, 124.3, 128.7, 128.8, 129.1, 129.2, 129.2, 129.2, 158.5, 160.9 ppm. HRMS (ESI): calcd. for C_7H_7FO $[M + H]^+$ 127.0481; found 127.0479.

2-Chloro-4-fluorobenzyl Alcohol ($2a_{23}$):[22] According to GP-I, 2-chloro-4-fluorobenzaldehyde (**$1a_{23}$**) (158 mg, 1.0 mmol, 1.0 equiv.) afforded **$2a_{23}$** (140 mg, 87 %) as a colorless liquid. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 4.53 (d, J = 5.0 Hz, 2 H), 5.39 (t, J = 5.7 Hz, 1 H), 7.32–7.25 (m, 2 H), 7.48 (t, J = 8.2 Hz, 1 H) ppm. ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 56.4, 56.4, 115.3, 115.6, 124.5, 128.4, 128.5, 130.2, 130.3, 132.1, 132.2, 158.3, 160.8 ppm. HRMS (ESI): calcd. for C_7H_6FClO $[M + H]^+$ 161.5733; found 161.5734.

3,4-Difluorobenzyl Alcohol ($2a_{24}$):[23] According to GP-I, 3,4-difluorobenzaldehyde (**$1a_{24}$**) (142 mg, 1.0 mmol, 1.0 equiv.) afforded **$2a_{24}$** (128 mg, 90 %) as a colorless liquid. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 4.46 (d, J = 6.3 Hz, 2 H), 5.39 (t, J = 6.3 Hz, 1 H), 7.13–7.11 (m, 1 H), 7.40–7.37 (m, 2 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 61.8, 115.1, 115.3, 116.9,117.1, 122.8, 122.8, 122.8, 122.9, 140.4, 140.5, 140.6, 147.1, 147.2, 148.2, 148.3, 149.5, 149.6, 150.6, 150.7 ppm. HRMS (ESI): calcd. for $C_7H_6F_2O$ $[M + H]^+$ 145.0387; found 145.0389.

1-Naphthalenylmethanol ($2a_{25}$):[6j] According to GP-I, 1-naphthaldehyde (**$1a_{25}$**) (156 mg, 1.0 mmol, 1.0 equiv.) afforded **$2a_{25}$** (136 mg, 86 %) as a colorless liquid. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 4.94 (d, J = 4.2 Hz, 2 H), 5.30 (br. s, 1 H), 7.39–7.54 (m, 4 H), 7.75 (d, J = 7.9 Hz, 1 H), 7.85 (d, J = 8.6 Hz, 1 H), 8.04 (d, J = 7.3 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 61.2, 123.7, 124.2, 125.4, 125.6, 125.9, 127.3, 128.3, 130.7, 133.2, 137.8 ppm. HRMS (ESI): calcd. for $C_{11}H_{10}O$ $[M + H]^+$ 159.0732; found 159.0730.

2-Naphthalenylmethanol ($2a_{26}$):[6d] According to GP-I, 2-naphthaldehyde (**$1a_{26}$**) (156 mg, 0.50 mmol, 1.0 equiv.) afforded **$2a_{26}$** (136 mg, 86 %) as a colorless liquid. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 5.65 (d, J = 5.7 Hz, 2 H), 5.37 (t, J = 5.7 Hz, 1 H), 7.38–7.44 (m, 3 H), 7.78–7.82 (m, 4 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 63.2, 124.4, 125.4, 125.5, 126.1, 127.6, 127.7, 132.3, 133.1, 140.3 ppm. HRMS (ESI): calcd. for $C_{11}H_{10}O$ $[M + H]^+$ 159.0732; found 159.0731.

(4,8-Dihydropyren-1-yl)methanol ($2a_{27}$):[24] According to GP-I, pyrenecarbaldehyde (**$1a_{27}$**) (232 mg, 1.0 mmol, 1.0 equiv.) afforded **$2a_{27}$** (212 mg, 91 %) as a colorless liquid. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 1.98 (br. s, 1 H), 5.39 (s, 2 H), 7.99–8.05 (m, 4 H), 8.14 (t, J = 7.6 Hz, 2 H), 8.20 (t, J = 6.7 Hz, 2 H), 8.36 (d, J = 9.2 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 63.9, 123.3, 124.9, 125.1, 125.2, 125.5, 126.2, 126.3, 127.7, 128.1, 129.1, 131.1, 131.5, 130.9, 131.6, 134.3 ppm. HRMS (ESI): calcd. for $C_{17}H_{14}O$ $[M + H]^+$ 235.1045; found 235.1048.

Pyridin-4-ylmethanol ($2a_{28}$):[6k] According to GP-I, pyridine-4-carbaldehyde (**$1a_{28}$**) (106 mg, 1.0 mmol, 1.0 equiv.) afforded **$2a_{28}$** (96 mg, 88 %) as a colorless liquid. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 4.48 (d, J = 6.1 Hz, 2 H), 5.38 (t, J = 6.1 Hz, 1 H), 7.27 (d, J = 4.9 Hz, 2 H), 8.46 (d, J = 4.9 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 61.4, 121.1, 149.3, 151.5 ppm. HRMS (ESI): calcd. for C_6H_7NO $[M + H]^+$ 110.0528; found 110.0526.

Thiazol-2-ylmethanol ($2a_{29}$):[25] According to GP-I, thiazole-2-carbaldehyde (**$1a_{29}$**) (112 mg, 1.0 mmol, 1.0 equiv.) afforded **$2a_{29}$** (104 mg, 91 %) as a colorless liquid. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 4.64 (d, J = 5.9 Hz, 2 H), 5.9 (t, J = 5.9 Hz, 1 H), 7.55 (d, J = 3.4 Hz, 1 H), 8 (d, J = 3.4 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 60.9, 119.5, 142.3, 173.7 ppm. HRMS (ESI): calcd. for C_4H_5NOS $[M + H]^+$ 116.0092; found 116.0090.

Furan-2-ylmethanol ($2a_{30}$):[6b] According to GP-I, furan-2-carbaldehyde (**$1a_{30}$**) (96 mg, 1.0 mmol, 1.0 equiv.) afforded **$2a_{30}$** (88 mg, 90 %) as a colorless liquid. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 4.64 (d, J = 5.9 Hz, 2 H), 5.9 (t, J = 5.9 Hz, 1 H), 7.55 (d, J = 3.4 Hz, 1 H), 8 (d, J = 3.4 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 55.7, 106.9, 110.3, 142.1, 155.5 ppm. HRMS (ESI): calcd. for $C_5H_6O_2$ $[M + H]^+$ 99.0368; found 99.0367.

9-[3-(Dimethylamino)propyl]-6-(hydroxymethyl)-9*H*-carbazole-3-carbaldehyde ($2a_{31}$): According to GP-I, 9-[3-(dimethylamino)-propyl]-9*H*-carbazole-3,6-dicarbaldehyde (**$1a_{31}$**) (308 mg, 1.0 mmol, 1.0 equiv.) afforded **$2a_{31}$** (304 mg, 98 %) as a pale yellow liquid. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 1.92 (t, J = 6.8 Hz, 2 H), 2.12 (s, 6 H), 2.19 (t, J = 6.7 Hz, 2 H), 4.80 (t, J = 6.7 Hz, 2 H), 4.68 (s, 2 H), 5.22 (br. s, 1 H), 7.51 (d, J = 8.4 Hz, 1 H), 7.66 (d, J = 8.4 Hz, 2 H), 7.76 (d, J = 8.4 Hz, 1 H), 7.98 (d, J = 10.1 Hz, 1 H), 8.21 (s, 1 H), 8.74 (s, 1 H), 10.06 (s, 1 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 26.3,

40.5, 45.0, 55.8, 63.3, 109.7, 109.8, 118.1, 122.0, 122.2, 124.1, 126.0, 126.2, 128.2, 134.6, 140.0, 143.8, 191.8 ppm. HRMS (ESI): calcd. for $C_{19}H_{22}N_2O_2$ $[M + H]^+$ 311.1681; found 311.1682.

{9-[3-(Dimethylamino)propyl]-9*H*-carbazole-3,6-diyl}-dimethanol (2a$_{32}$): According to GP-I, 9-[3-(dimethylamino)propyl]-9*H*-carbazole-3,6-dicarbaldehyde (**1a$_{31}$**) (308 mg, 1.0 mmol, 1.0 equiv.) afforded **2a$_{32}$** (294 mg, 90 %) as a pale yellow liquid. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 1.92 (t, J = 6.8 Hz, 2 H), 2.15 (s, 6 H), 2.19 (t, J = 6.8 Hz, 2 H), 4.42 (t, J = 6.4 Hz, 2 H), 4.75 (d, J = 3.0 Hz, 4 H), 5.27 (br. s, 2 H), 7.48 (d, J = 9.3 Hz, 2 H), 7.57 (d, J = 8.3 Hz, 2 H), 8.15 (s, 2 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 26.5, 39.3, 45.0, 56.0, 63.6, 108.7, 118.4, 121.9, 125.0, 126.2, 132.9, 139.6 ppm. HRMS (ESI): calcd. for $C_{19}H_{24}N_2O_2$ $[M + H]^+$ 313.1838; found 313.1838.

(*R*)-3-(1-Benzyl-1*H*-indol-3-yl)butan-1-ol (2a$_{33}$): According to GP-I, (*R*)-3-(1-benzyl-1*H*-indol-3-yl)butanal (**1a$_{32}$**) (276 mg, 1.0 mmol, 1.0 equiv.) afforded **2a$_{33}$** (256 mg, 92 %) as a brown liquid. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 1.40 (d, J = 6.7 Hz, 3 H), 1.96–1.92 (m, 1 H), 2.08–2.03 (m, 1 H), 3.26–3.22 (m, 1 H), 3.70–3.66 (m, 2 H), 5.28 (s, 2 H), 6.92 (s, 1 H), 7.13–7.10 (m, 3 H), 7.17 (t, J = 6.7 Hz, 1 H), 7.31–7.25 (m, 4 H), 7.68 (d, J = 8.4 Hz, 1 H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ = 22.0, 27.9, 40.6, 50.0, 61.8, 109.9, 119.0, 119.7, 121.1, 121.9, 124.5, 126.8, 127.5, 127.7, 128.9, 137.1, 137.9 ppm. HRMS (ESI): calcd. for $C_{19}H_{21}NO$ $[M + H]^+$ 280.1623; found 280.1622.

(*E*)-Cinnamyl Alcohol (2a$_{34}$):[6f] According to GP-I, (*E*)-cinnamaldehyde (**1a$_{33}$**) (132 mg, 1.0 mmol, 1.0 equiv.) afforded **2a$_{34}$** (130 mg, 98 %) as a white solid. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 4.06–4.09 (m, 2 H), 4.82 (t, J = 5.5 Hz, 1 H), 6.30–6.36 (m, 1 H), 6.51 (d, J = 15.8 Hz, 1 H), 7.18 (t, J = 7.32 Hz, 1 H), 7.28 (t, J = 7.3 Hz, 2 H), 7.37 (d, J = 7.3 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 61.4, 126.0, 127.1, 128.4, 128.3, 130.7, 136.9 ppm. HRMS (ESI): calcd. for $C_9H_{10}O$ $[M + H]^+$ 135.0732; found 135.0736.

(3-Phenyloxiran-2-yl)methanol (2a$_{35}$):[6f] According to GP-I, 3-phenyloxirane-2-carbaldehyde (**1a$_{34}$**) (148 mg, 1.0 mmol, 1.0 equiv.) afforded **2a$_{35}$** (140 mg, 92 %) as a colourless liquid. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 2.67 (br. s, 1 H), 3.23–3.21 (m, 1 H), 3.76 (d, J = 11.2 Hz, 1 H), 3.91 (d, J = 2.0 Hz, 1 H), 4.02 (d, J = 12.7 Hz, 1 H), 7.36–7.25 (m, 5 H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 55.8, 61.4, 62.7, 125.8, 128.4, 128.6, 136.7 ppm. HRMS (ESI): calcd. for $C_9H_{10}O_2$ $[M + H]^+$ 151.0681; found 151.0680.

(Cyclohex-3-en-1-yl)methanol (2a$_{36}$):[26] According to GP-I, 3-cyclohexenecarbaldehyde (**1a$_{35}$**) (110 mg, 1.0 mmol, 1.0 equiv.) afforded **2a$_{36}$** (88 mg, 78 %) as a colorless liquid. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 1.23–1.15 (m, 1 H), 1.70–1.62 (m, 2 H), 1.78–1.75 (m, 1 H), 2.06–1.98 (m, 3 H), 3.34–3.29 (m, 2 H), 4.52 (t, J = 5.0 Hz, 1 H), 5.66 (s, 2 H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 24.3, 25.1, 27.9, 36.1, 65.8, 126.3, 126.9 ppm. HRMS (ESI): calcd. for $C_7H_{12}O$ $[M + H]^+$ 113.1045; found 113.1044.

Cyclohexylmethanol (2a$_{37}$):[6f] According to GP-I, cyclohexanecarbaldehyde **1a$_{36}$** (112 mg, 1.0 mmol, 1.0 equiv.) afforded **2a$_{37}$** (88 mg, 78 %) as a colorless liquid. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 0.87–0.95 (m, 2 H), 1.11–1.28 (m, 3 H), 1.43–1.50 (m, 1 H), 1.65–1.75 (m, 5 H), 2.0 (t, J = 11.4 Hz, 1 H), 3.40 (d, J = 3.3 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 26.1, 26.8, 29.8, 40.7, 68.9 ppm. HRMS (ESI): calcd. for $C_7H_{14}O$ $[M + H]^+$ 115.1045; found 115.1042.

Ethanol (2a$_{38}$): According to GP-I, acetaldehyde (**1a$_{37}$**) (44 mg, 1.0 mmol, 1.0 equiv.) afforded **2a$_{38}$** (38 mg, 84 %) as a colorless liquid. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 0.85 (t, J = 6.9 Hz, 3 H), 3.28–3.33 (m, 2 H), 4.60 (t, J = 4.4 Hz, 1 H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ = 17.5, 57.1 ppm. HRMS (ESI): calcd. for C_2H_6O $[M + H]^+$ 47.0419; found 47.0416.

Hexan-1-ol (2a$_{39}$):[6b] According to GP-I, hexanal (**1a$_{38}$**) (100 mg, 1.0 mmol, 1.0 equiv.) afforded **2a$_{39}$** (82 mg, 80 %) as a colorless liquid. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 0.87–0.85 (m, 3 H), 1.30–1.22 (m, 6 H), 1.43–1.37 (m, 2 H), 3.39–3.35 (m, 2 H), 4.31 (t, J = 5.7 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 13.8, 22.1, 25.2, 31.2, 32.5, 60.7 ppm. HRMS (ESI): calcd. for $C_6H_{14}O$ $[M + H]^+$ 103.1045; found 103.1039.

1-Phenylethanol (5a):[6e] According to GP-II, acetophenone (**4a**) (120 mg, 1.0 mmol, 1.0 equiv.) afforded **5a** (92 mg, 75 %) as a colorless liquid. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 1.29 (d, J = 6.7 Hz, 3 H), 4.70 (t, J = 4.9 Hz, 1 H), 5.12 (d, J = 3.6 Hz, 1 H), 7.16 (t, J = 6.7 Hz, 1 H), 7.33–7.25 (m, 4 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 25.9, 68.2, 125.3, 126.5, 127.9, 147.4 ppm. HRMS (ESI): calcd. for $C_8H_{10}O$ $[M + H]^+$ 123.0732; found 123.0730.

1-(*p*-Tolyl)ethanol (5b):[27] According to GP-II, 4-methylacetophenone (**4b**) (134 mg, 1.0 mmol, 1.0 equiv.) afforded **5b** (100 mg, 73 %) as a pale yellow liquid. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 1.20 (t, J = 3.8 Hz, 3 H), 2.15 (s, 3 H), 4.55–4.59 (m, 1 H), 4.95 (d, J = 4.4 Hz, 1 H), 6.97 (d, J = 7.6 Hz, 2 H), 7.10 (d, J = 7.6 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 20.6, 25.9, 67.9, 125.2, 128.5, 135.4, 143.4 ppm. HRMS (ESI): calcd. for $C_9H_{12}O$ $[M + H]^+$ 137.0888; found 137.0884.

1-(4-Bromophenyl)ethanol (5c):[6d] According to GP-II, 4-bromoacetophenone (**4c**) (200 mg, 1.0 mmol, 1.0 equiv.) afforded **5c** (164 mg, 82 %) as a straw-yellow liquid. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 1.22 (d, J = 6.7 Hz, 3 H), 4.62–4.65 (m, 1 H), 5.16 (d, J = 4.3 Hz, 1 H), 7.22 (d, J = 8.5 Hz, 2 H), 7.41 (dd, J = 1.8, 6.9 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 25.7, 67.4, 119.3, 127.5, 130.8, 146.7 ppm. HRMS (ESI): calcd. for C_8H_9BrO $[M + H]^+$ 200.9837; found 200.9834.

4-(1-Hydroxyethyl)phenol (5d):[28] According to GP-II, 4-hydroxyacetophenone (**4d**) (136 mg, 1.0 mmol, 1.0 equiv.) afforded **5d** (106 mg, 77 %) as a colorless liquid. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 1.21 (d, J = 6.1 Hz, 3 H), 4.52–4.56 (m, 1 H), 4.85 (d, J = 3.6 Hz, 1 H), 6.63 (dd, J = 1.8, 6.7 Hz, 2 H), 7.06 (t, J = 7.9 Hz, 2 H), 9.12 (s, 1 H) ppm. ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 25.9, 67.7, 114.6, 126.4, 137.6, 159.9 ppm. HRMS (ESI): calcd. for $C_8H_{10}O_2$ $[M + H]^+$ 139.0681; found 139.0679.

1-(4-Methoxyphenyl)ethanol (5e):[6e] According to GP-II, 4-methoxyacetophenone (**4e**) (150 mg, 1.0 mmol, 1.0 equiv.) afforded **5e** (112 mg, 74 %) as a colorless liquid. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 1.23 (d, J = 5.9 Hz, 3 H), 3.65 (d, J = 10.0 Hz, 3 H), 4.60 (d, J = 3.4 Hz, 1 H), 4.94 (d, J = 2.5 Hz, 1 H), 6.78 (t, J = 5.0 Hz, 2 H), 7.17 (t, J = 5.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 25.9, 55.0, 67.7, 113.3, 126.4, 139.4, 158.0 ppm. HRMS (ESI): calcd. for $C_9H_{12}O_2$ $[M + H]^+$ 153.0837; found 153.0834.

1-(4-Aminophenyl)ethanol (5f):[6e] According to GP-II, 4-aminoacetophenone (**4f**) (135 mg, 1.0 mmol, 1.0 equiv.) afforded **5f** (114 mg, 80 %) as a deep-brown liquid. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 1.26 (d, J = 5.9 Hz, 3 H), 4.57–4.52 (m, 1 H), 4.79 (d, J = 2.5 Hz, 1 H), 4.87 (br. s, 2 H), 6.50 (d, J = 8.4 Hz, 2 H), 6.98 (d, J = 8.4 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 25.8, 67.9, 113.5, 126.0, 134.6, 147.2 ppm. HRMS (ESI): calcd. for $C_8H_{11}NO$ $[M + H]^+$ 138.0841; found 138.0843.

2,2,2-Trifluoro-1-phenylethanol (5g):[6e] According to GP-II, 2,2,2-trifluoroacetophenone (**4g**) (174 mg, 1.0 mmol, 1.0 equiv.) afforded **5g** (152 mg, 84 %) as a colorless liquid. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 5.17 (q, J = 7.3 Hz, 1 H), 7.44–7.38 (m, 3 H), 7.54 (d, J = 6.7 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 70.4, 70.7, 71.0, 71.3, 123.8, 126.7, 127.7, 128.3, 128.9, 136.1 ppm. HRMS (ESI): calcd. for $C_8H_7F_3O$ $[M + H]^+$ 177.0449; found 177.0450.

Diphenylmethanol (5h):[6j] According to GP-II, benzophenone (**4h**) (182 mg, 1.0 mmol, 1.0 equiv.) afforded **5f** (175 mg, 95 %) as a white solid. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 5.64 (d, J = 6.9 Hz, 1 H), 5.81 (d, J = 3.8 Hz, 1 H), 7.15–7.12 (m, 2 H), 7.25–7.22 (m, 2 H), 7.31 (d, J = 6.9 Hz, 4 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 74.2, 126.2, 126.6, 128.0, 145.7 ppm. HRMS (ESI): calcd. for $C_{13}H_{12}O$ [M + H]$^+$ 185.0888; found 185.0886.

1,2-Diphenylpent-4-ene-1,2-diol (5i):[29] According to GP-II, 2-hydroxy-1,2-diphenyl-4-penten-1-one (**4i**) (252 mg, 1.0 mmol, 1.0 equiv.) afforded **5i** (204 mg, 80 %) as a white solid. ^{1}H NMR of *syn* isomer (400 MHz, CDCl$_3$): δ = 2.53 (br. s, 2 H), 2.76 (dd, J = 4.9, 9.2 Hz,1 H) 2.94 (dd, J = 5.5, 8.7 Hz, 1 H), 4.79 (s, 1 H), 5.09 (d, J = 10.3 Hz, 1 H), 5.17 (d, J = 17.1 Hz, 1 H), 5.63–5.52 (m, 1 H), 6.99 (dd, J = 1.2, 6.1 Hz, 2 H), 7.21–7.12 (m, 8 H) ppm. ^{13}C NMR of *syn* isomer (100 MHz, CDCl$_3$): δ = 42.7, 78.5, 80.6, 119.9, 126.7, 127.0, 127.6, 127.7, 127.9, 128.8, 133.5, 139.5, 141.7 ppm. HRMS (ESI): calcd. for $C_{17}H_{18}O_2$ [M + H]$^+$ 255.1307; found 255.1309.

1,2-Diphenylethane-1,2-diol (5j):[10c] According to GP-II, 2-hydroxy-1,2-diphenylethanone (**4j**) (212 mg, 1.0 mmol, 1.0 equiv.) afforded **5j** (184 mg, 86 %) as a white solid. ^{1}H NMR of *dl* isomer (500 MHz, [D$_6$]DMSO): δ = 4.57 (d, J = 1.3 Hz, 2 H), 5.19 (d, J = 1.2 Hz, 2 H), 7.24–7.18 (m, 10 H) ppm. ^{13}C NMR of *dl* isomer (100 MHz, [D$_6$]DMSO): δ = 76.9, 126.5, 127.2, 127.3, 143.2 ppm. HRMS (ESI): calcd. for $C_{14}H_{14}O_2$ [M + H]$^+$ 215.0994; found 215.0991.

1,2-Diphenylethane-1,2-diol (5j):[10c] According to GP-II, benzil (**4k**) (210 mg, 1.0 mmol, 1.0 equiv.) afforded **5j** (176 mg, 82 %) as a white solid.

(*E*)-1,3-Diphenylprop-2-en-1-ol (5k): According to GP-II, (*E*)-chalcone (**4l**) (208 mg, 1.0 mmol, 1.0 equiv.) afforded **5k** (194 mg, 86 %) as a white solid. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 5.25 (t, J = 5.5 Hz, 1 H), 5.62 (d, J = 4.2 Hz, 1 H), 6.39 (dd, J = 6.1, 9.8 Hz, 1 H), 6.63 (d, J = 15.9 Hz, 1 H), 7.24 (dd, J = 7.9, 8.0 Hz, 2 H), 7.36–7.29 (m, 4 H), 7.41 (t, J = 6.70 Hz, 4 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 73.1, 126.1, 126.2, 126.8, 126.7, 128.1, 128.5, 133.6, 136.6, 144.4 ppm. HRMS (ESI): calcd. for $C_{15}H_{14}O$ [M + H]$^+$ 211.1045; found 211.1044.

Phenyl(3-phenyloxiran-2-yl)methanol (5l): According to GP-II, phenyl(3-phenyloxiran-2-yl)methanone (**4m**) (224 mg, 1.0 mmol, 1.0 equiv.) afforded **5l** (208 mg, 88 %) as a colourless liquid. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 2.66 (br. s, 1 H), 3.31–3.29 (m, 1 H), 4.01 (d, J = 2.0 Hz, 1 H), 4.72 (s, 1 H), 7.25 (d, J = 7.3 Hz, 2 H), 7.35–7.29 (m, 4 H), 7.38 (t, J = 6.9 Hz, 2 H), 7.43 (t, J = 7.4 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 57.0, 65.8, 73.5, 125.9, 126.3, 126.7, 128.4, 128.5, 128.7, 128.9, 136.5, 140.3 ppm. HRMS (ESI): calcd. for $C_{15}H_{14}O_2$ [M + H]$^+$ 227.0994; found 227.0993.

1-(Pyridin-2-yl)ethanol (5m):[27] According to GP-II, 2-acetylpyridine (**4n**) (120 mg, 1.0 mmol, 1.0 equiv.) afforded **5m** (98 mg, 80 %) as a pale yellow liquid. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 1.44 (d, J = 6.7 Hz, 3 H), 4.85–4.79 (m, 1 H), 5.46 (d, J = 4.3 Hz, 1 H), 7.31–7.28 (m, 1 H), 7.60 (d, J = 7.9 Hz, 1 H), 7.86–7.82 (m, 1 H), 8.55–8.54 (m, 1 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 24.2, 69.4, 119.3, 121.8, 136.6, 148.2, 165.6 ppm. HRMS (ESI): calcd. for C_7H_9NO [M + H]$^+$ 124.0684; found 124.0680.

Ethyl 3-Hydroxybutanoate (5n): According to GP-II, ethyl 3-oxobutanoate (**4o**) (130 mg, 1.0 mmol, 1.0 equiv.) afforded **5n** (104 mg, 74 %) as a colorless liquid. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 1.00 (d, J = 6.1 Hz, 3 H), 1.09 (t, J = 6.7 Hz, 3 H), 2.25 (t, J = 7.9 Hz, 2 H), 3.49 (s, 1 H), 3.98–3.90 (m, 2 H), 4.63 (d, J = 4.9 Hz, 1 H) ppm. ^{13}C MNR (125 MHz, [D$_6$]DMSO): δ = 14.1, 22.3, 43.9, 59.6, 63.4, 171.1 ppm. HRMS (ESI): calcd. for $C_6H_{12}O_3$ [M + H]$^+$ 133.0786; found 133.0788.

Cyclohexanol (5o):[6e] According to GP-II, cyclohexanone (**4p**) (98 mg, 1.0 mmol, 1.0 equiv.) afforded **5o** (74 mg, 74 %) as a colorless liquid. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 0.97–1.11 (m, 5 H), 1.35 (t, J = 4.2 Hz, 1 H), 1.55 (s, 2 H), 1.70 (s, 2 H), 3.37 (s, 1 H), 3.74 (br. s, 1 H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ = 24.0, 25.3, 35.1, 69.6 ppm. HRMS (ESI): calcd. for $C_6H_{12}O$ [M + H]$^+$ 101.0888; found 101.0883.

Cyclopentanol (5p):[30] According to GP-II, cyclopentanone (**4q**) (84 mg, 1.0 mmol, 1.0 equiv.) afforded **5p** (64 mg, 74 %) as a colorless liquid. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 1.46–1.50 (m, 4 H), 1.66 (t, J = 1.9 Hz, 4 H), 2.89–3.04 (m, 1 H), 4.19 (br. s, 1 H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 23.2, 35.3, 73.6 ppm. HRMS (ESI): calcd. for $C_5H_{10}O$ [M + H]$^+$ 87.0732; found 87.0728.

Propan-2-ol (5q): According to GP-II, acetone (**4r**) (60 mg, 0.50 mmol, 1.0 equiv.) afforded **5q** (44 mg, 72 %) as a colorless liquid. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 1.0–1.05 (m, 6 H), 3.31–3.68 (m, 1 H), 3.83 (br. s, 1 H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 25.0, 63.7 ppm. HRMS (ESI): calcd. for C_3H_8O [M + H]$^+$ 61.0575; found 61.0574.

2,3-Diphenylbutane-2,3-diol (6a):[9] According to GP-II, acetophenone (**4a**) (120 mg, 1.0 mmol, 1.0 equiv.) afforded **6a** (54 mg, 23 %) as a white solid. ^{1}H NMR (*dl*/*meso* = 60:40) (500 MHz, CDCl$_3$): δ = 1.49 (s, 6 H), 1.57 (s, 6 H), 2.33 (s, 2 H), 2.64 (s, 2 H), 7.17–7.25 (m, 20 H) ppm. ^{13}C NMR (*dl*/*meso* = 60:40) (100 MHz, CDCl$_3$): δ = 25.1, 25.2, 78.7, 78.9, 127.5, 127.4, 127.3, 127.2, 127.1, 127.0, 143.6, 143.9 ppm. HRMS (ESI): calcd. for $C_{16}H_{18}O_2$ [M + H]$^+$ 243.1207; found 243.1205.

2,3-Di-*p*-tolylbutane-2,3-diol (6b):[9] According to GP-II, 4-methylacetophenone (**4b**) (134 mg, 1.0 mmol, 1.0 equiv.) afforded **6b** (70 mg, 26 %) as a white solid. ^{1}H NMR (*dl*/*meso* = 60:40): δ = (500 MHz, CDCl$_3$): δ = 1.46 (s, 6 H), 1.53 (s, 6 H), 2.32 (d, J = 6.7 Hz, 12 H), 2.23 (br. s, 2 H), 2.58 (br. s, 2 H), 7.09–7.04 (m, 14 H, 7.14 (d, J = 7.6 Hz, 2 H) ppm. ^{13}C NMR (*dl*/*meso* = 60:40) (100 MHz, CDCl$_3$): δ = 21.0, 21.1, 25.2, 25.4, 78.7, 78.9, 127.0, 127.4, 128.0, 128.1, 136.5, 136.7, 140.7, 141.1 ppm. HRMS (ESI): calcd. for $C_{18}H_{22}O_2$ [M + H]$^+$ 271.1620; found 271.1618.

1-[4-(Hydroxymethyl)phenyl]ethanone (8):[6h] According to GP-I, 4-acetylbenzaldehyde (**7**) (148 mg, 1.0 mmol, 1.0 equiv.) afforded **8** (144 mg, 96 %) as a colorless liquid. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 2.52 (s, 3 H), 4.53 (d, J = 5.9 Hz, 2 H), 5.32 (t, J = 5.9 Hz, 1 H), 7.41 (d, J = 8.1 Hz, 2 H), 7.87 (dd, J = 1.8, 4.4 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 26.7, 62.5, 126.3, 128.2, 135.5, 148.2, 197.6 ppm. HRMS (ESI): calcd. for $C_9H_{10}O_2$ [M + H]$^+$ 151.0681; found 151.0684.

1-[4-(Hydroxymethyl)phenyl]ethanol (9):[31] According to GP-II, 4-acetylbenzaldehyde (**7**) (148 mg, 1.0 mmol, 1.0 equiv.) afforded **9** (124 mg, 82 %) as a brown liquid. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 1.13 (d, J = 6.1 Hz, 3 H), 4.29 (d, J = 5.9 Hz, 2 H), 4.49–4.51 (m, 1 H), 4.92–4.96 (m, 2 H), 7.08 (dd, J = 8.0, 7.9 Hz, 4 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 26.1, 63.0, 68.1, 125.1, 126.3, 140.8, 145.9 ppm. HRMS (ESI): calcd. for $C_9H_{12}O_2$ [M + H]$^+$ 153.0837; found 153.0835.

1-[4-(Hydroxymethyl)phenyl]ethanol (9):[31] According to GP-II, 1-[4-(hydroxymethyl)phenyl]ethanone (**8**) (150 mg, 1.0 mmol, 1.0 equiv.) afforded **9** (130 mg, 86 %) as a brown liquid.

3-Hydroxyindolin-2-one (11a):[18b] According to GP-III, isatin (**10a**) (148 mg, 1.0 mmol, 1.0 equiv.) afforded **11a** (140 mg, 94 %) as a white solid. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 3.18 (br. s, 1 H), 5.08 (s, 1 H), 6.86 (d, J = 7.6 Hz, 1 H), 7.09 (t, J = 7.5 Hz, 1 H), 7.28 (d, J = 7.6 Hz, 1 H), 7.44 (d, J = 6.9 Hz, 1 H) ppm. ^{13}C NMR (100 MHz,

$CDCl_3$): δ = 70.3, 110.4, 123.5, 125.8, 130.2, 138.8, 141.1, 178.4 ppm. HRMS (ESI): calcd. for $C_8H_7NO_2$ $[M + H]^+$ 150.0477; found 150.0467.

3-Hydroxy-1-methylindolin-2-one (11b):[18b] According to GP-III, *N*-methylisatin (**10b**) (160 mg, 1.0 mmol, 1.0 equiv.) afforded **11b** (160 mg, 98 %) as a pale-yellow solid. ^{1}H NMR (500 MHz, [D_6]DMSO): δ = 2.98 (s, 3 H), 4.80 (d, *J* = 7.6 Hz, 1 H), 6.15 (d, *J* = 7.1 Hz, 1 H), 6.84 (d, *J* = 7.6 Hz, 1 H), 6.95 (t, *J* = 6.7 Hz, 1 H), 7.25–7.19 (m, 2 H) ppm. ^{13}C NMR (100 MHz, [D_6]DMSO): δ = 25.7, 68.7, 108.3, 122.1, 124.4, 128.5, 129.0, 143.7, 175.9 ppm. HRMS (ESI): calcd. for $C_9H_9NO_2$ $[M + H]^+$ 164.0633; found 164.0631.

1-Benzyl-5-chloro-3-hydroxyindolin-2-one (11c): According to GP-III, *N*-benzyl-5-chloroisatin (**10c**) (270 mg, 1.0 mmol, 1.0 equiv.) afforded **11c** (268 mg, 98 %) as a white solid. ^{1}H NMR (500 MHz, [D_6]DMSO): δ = 4.80 (s, 2 H), 5.05 (d, *J* = 7.6 Hz, 1 H), 6.48 (d, *J* = 7.6 Hz, 1 H), 6.79 (d, *J* = 7.5 Hz, 1 H), 7.28–7.16 (m, 6 H), 7.33 (s, 1 H) ppm. ^{13}C NMR (125 MHz, [D_6]DMSO): δ = 42.6, 68.7, 110.5, 124.2, 126.6, 126.9, 127.2, 127.4, 128.7, 130.8, 135.9, 141.5, 175.8 ppm. HRMS (ESI): calcd. for $C_{15}H_{12}ClNO_2$ $[M + H]^+$ 274.0557; found 274.0564.

1-Benzyl-5-fluoro-3-hydroxyindolin-2-one (11d): According to GP-III, *N*-benzyl-5-fluoroisatin (**10d**) (254 mg, 1.0 mmol, 1.0 equiv.) afforded **11d** (254 mg, 99 %) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.79 (dd, *J* = 15.2, 15.3 Hz, 2 H), 5.23 (s, 1 H), 5.59 (br. s, 1 H), 6.56 (dd, *J* = 4.9, 3.7 Hz, 1 H), 6.83 (t, *J* = 9.1 Hz, 1 H), 7.27–7.15 (m, 6 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 44.0, 69.9, 110.1, 110.2, 113.3, 113.5, 115.6, 115.8, 117.0, 117.2, 127.0, 127.3, 127.7, 127.9, 128.8, 128.9, 129.1, 129.2, 134.5, 135.0, 138.6, 139.4, 158.4, 160.8, 177.6 ppm. HRMS (ESI): calcd. for $C_{15}H_{10}FNO_2$ $[M + H]^+$ 258.0696; found 258.0698.

1-Benzyl-3-hydroxy-5-(trifluoromethoxy)indoline-2-one (11e): According to GP-III, *N*-benzyl-5-(trifluoromethoxy)isatin (**10e**) (320 mg, 1.0 mmol, 1.0 equiv.) afforded **11e** (310 mg, 96 %) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.62 (s, 1 H), 4.79 (dd, *J* = 15.8, 15.1 Hz, 2 H), 5.12 (s, 1 H), 6.61 (d, *J* = 8.4 Hz, 1 H), 7.00 (d, *J* = 8.4 Hz, 1 H), 7.29–7.18 (m, 6 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 44.2, 69.8, 110.2, 119.4, 123.0, 124.1, 127.2, 127.4, 127.8, 127.9, 128.2, 128.6, 128.7, 129.0, 129.1, 134.4, 134.9, 141.0, 141.6, 142.2, 145.4, 177.2 ppm. HRMS (ESI): calcd. for $C_{16}H_{10}F_3NO_3$ $[M + H]^+$ 324.0613; found 324.0603.

Radical Quenching Experiment: To a stirred solution of 4-methylbenzaldehyde (**1a$_1$**) (1.0 mmol) in THF were added Zn dust (5.0 mmol), aqueous NH_4Cl (8 M) solution, and TEMPO or Galvinoxyl (1 mmol) at the same time. The reaction mixture was stirred at room temperature for 30 min. No product formation was observed.

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