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Domino Grignard Addition and Oxidation for the One-Pot Synthesis of C2-Quaternary 2-Hydroxyindoxyls

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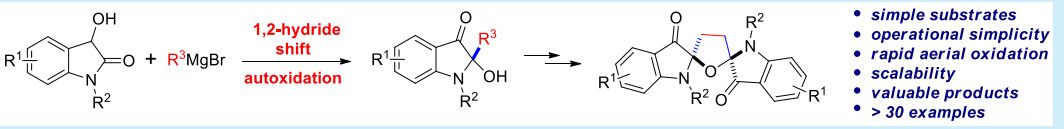
Supporting Information



ABSTRACT: We herein delineate an unexplored reactivity of 3-hydroxyoxindoles toward Grignard addition enabling a rapid access to a broad range of unnatural C2-quaternary 2-hydroxyindoxyls in high yields. The reaction proceeds via a mechanistically intriguing one-pot 1,2-hydride shift followed by autoxidation pathway. The utility of this method is demonstrated by the synthesis of a new class of bis-indoxyl spirofuran derivatives.

The oxindole moiety is present in a large number of natural products and biologically active molecules.[1] The motif has also been used as a versatile synthetic intermediate for various organic transformations.[1,2] On the contrary, 2-hydroxyindoxyl, a pseudooxindole moiety, has remained less explored. The indoxyl ring system bearing a C2-quaternary center is a privileged structural unit present in various natural products like brevianamide A and B,[3] rupicoline,[4] iboluteine,[5] austamide,[6] phytoaliexin, erucalexin,[7] and matemone,[8] as well as biologically active compounds (Figure 1). For instance, 2-hydroxyindoxyl alkaloid melochicorin, isolated from the plant *Melochia corchorifolia*,[9] shows hepatoprotective and antioxidant activity.[10]

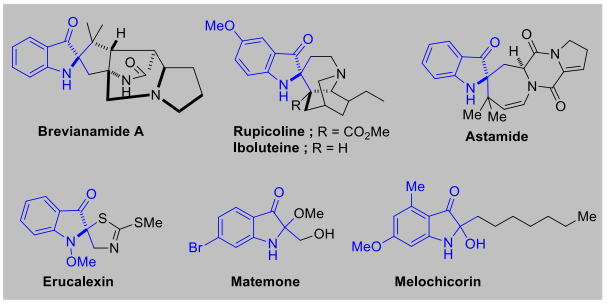


Figure 1. Some biologically active indoxyl derivatives.

While 3-substituted 3-hydroxy-2-oxindoles can be easily synthesized by reported methods,[11] the preparation of unnatural 2-substituted 2-hydroxyindoxyls remains a synthetic challenge. Until now, only a few convenient methods are available for the synthesis of pseudooxindole 2-hydroxyindoxyls. Generally, oxidation of indoles using *m*-CPBA,[12] monoperphthalic acid,[13] and DMDO[14] produces 2-hydroxyindoxyls as byproducts. Davis' reagent has been used to improve the yield of 2-hydroxyindoxyls.[15] Sakamoto et al.[16] reported oxidation of 2-substituted *N*-acylindoles by MoO_5·HMPA to directly obtain 1-acetyl-2-hydroxyindoxyls. Later, Jimenez et al. used oxodiperoxo molybdenum complexes to improve the yield.[17] The oxidation of 2,3,6-trimethyl-4-(1*H*)-quinolinone by NaOCl[18] and 2-methyl-3-phenylquinolinone by acidic potassium permanganate[19] has also been used to access the corresponding indoxyls. However, long reaction times and low yields render such approaches less attractive. Other reported approaches for the synthesis of 2-hydroxyindoxyls involve base-mediated ring contraction of 3-hydroxy-2,4(1*H*,3*H*)-quinolinediones,[20] acidic hydrolysis of a 3-acetoxy-2-phenylindole precursor,[21] butyllithium-promoted tandem cyclization, and autoxidation of 2-(benzylamino)-benzamide derivatives (Scheme 1).[22] Recently, Zhu and co-workers reported the synthesis of a 2-hydroxyindoxyl derivative by using a Cu(I)-catalyzed intramolecular C (sp3)−H amidation of 2-aminoacetophenone utilizing O_2 as the oxidant at high temperature (Scheme 1).[23] Later, Yang et al. developed an oxidative cyclization of 2-aminophenyl-1,3-dione using CAN and TEMPO as oxidants for the synthesis of 2-hydroxyindoline-3-ones (Scheme 1).[24] Nevertheless, the synthesis of 2-hydroxyindoxyls from readily available starting materials with high flexibility in their substitution pattern is yet to be addressed. Therefore, an easy-to-implement protocol to access a large panel of 2-indoxyl derivatives with a C2-quartenary tertiary alcohol moiety would be of great importance in synthetic organic chemistry.

Recently, we have reported the synthesis of 2,2-diallyloxindoles as well as substituted indole derivatives via the formation of indolinium ion intermediates using Grignard addition.[25] We envisioned that Grignard addition of 3-hydroxyoxindoles would lead to 2-substituted indoxyls via

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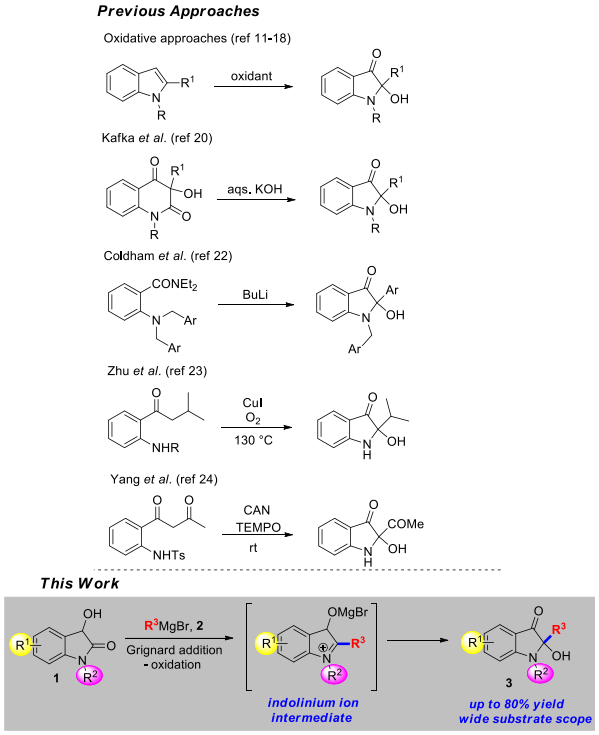
Org. Lett. XXXX, XXX, XXX−XXX

Scheme 1. Previous Study and Our Strategy

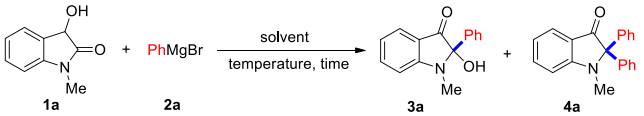


1,2-hydride shift of the indolinium ion intermediate which after air oxidation would provide the desired 2-hydroxyindoxyls (Scheme 1). This protocol will allow an easy access to 2-functionalized-2-hydroxyindoxyls starting from easily synthesizable starting materials with wide substrate scope.

In order to examine the feasibility of our proposed approach, a variety of *N*-protected 3-hydroxy-2-oxindoles **1** were prepared from *N*-protected isatin derivatives (see Scheme S1). We began the oxidative Grignard reaction with phenylmagnesium bromide **2a** (1 M in THF) addition to 3-hydroxy-1-methylindolin-2-one **1a**. We were delighted to find that the product **3a** was obtained in 60% yield along with **4a** as a minor product by using 3 equiv of **2a** in THF for 3 h at room temperature (Table 1, entry 1). Encouraged by this result, a systematic study was conducted to selectively obtain indoxyl derivative **3a**. Using 4 equiv of **2a**, the formation of **4a** was decreased, and the yield of **3a** was increased up to 68% (entry 2). The yield of **3a** was not improved further by increasing the amount of Grignard reagent **2a** (entry 3). However, by lowering the equivalence of **2a**, the yield of **3a** was decreased (entry 4). The yield of the desired product did not improve when the reaction was performed under reflux at 70 °C (entry 5). The yield of **3a** was dropped to 40% when the reaction was carried out at 0 °C (entry 6). By increasing the reaction time to 6 h, **3a** was obtained in 74% yield (entry 7). Carrying out the reaction for a prolonged time did not alter the outcome (entry 8). Further reaction optimization studies were then carried out by employing different solvents generally used in the Grignard reaction. The yield of **3a** was found to be decreased considerably by using diethyl ether, dioxane, or diglyme as the solvent instead of THF (entries 9−11). It is worth noting that the reaction could be scaled (1.0 g of **1a**) without a loss of yield under the ambient conditions (entry 12).

Having established the optimal reaction conditions, the scope and generality of this methodology was subsequently

Table 1. Reaction Development[a]



entry	2a (equiv)	solvent	temp (°C)	time (h)	conversion (3a/4a)[b]	yield of 3a[c] (%)
1	3	THF	25	3	80:20	60
2	4	THF	25	3	90:10	68
3	5	THF	25	3	90:10	67
4	2	THF	25	3	80:20	48
5	4	THF	70	3	90:10	66
6	4	THF	0	3	80:20	40
7	4	THF	25	6	90:10	74
8	4	THF	25	12	90:10	70
9	4	ether	25	6	80:20	42
10	4	dioxane	25	6	80:20	20
11	4	diglyme	25	6	80:20	Trace
12[d]	4	THF	25	6	90:10	72

[a]Reaction conditions: **1a** (1.0 equiv, 0.5 mmol), **2a** (1 M in THF). [b]Conversion is calculated by ^{1}H NMR analysis of crude reaction mixture. [c]Yield calculated are isolated yields. [d]Preparative-scale experiment.

explored for the synthesis of 2-hydroxyindoxyls **3**. Various functionalized 3-hydroxy-2-oxindoles **1** were subjected to the Grignard reaction with different aromatic and aliphatic Grignard reagents **2** (Table 2). The oxindoles having different *N*-substituents could be effectively converted to the corresponding products **3a**−**3f**, **3j**, and **3q**. Oxindoles bearing 4-trifluoromethylphenyl and propyl bromide groups as the *N*-substituent provided the indoxyls **3e** and **3f** in excellent yields. The reaction also worked well with the substrates having halides at different positions in the aromatic ring of the oxindole motif delivering the products **3g**−**3k** and **3u** with good yields. The structure of 2-hydroxyindoxyl **3g** was confirmed by single-crystal X-ray analysis (Table 2, CCDC 1919407; Figure S1). The 4,7-dichloro-3-hydroxyoxindole derivative provided the corresponding indoxyl **3i** in 64% yield. These halo indoxyls can be used as precursors for further synthetic transformations by cross-coupling reactions. Hydroxyindoxyls **3l**−**3p**, **3x**, and **3b′** having electron rich Me and OMe and electron deficient trifluoromethyl functional groups were obtained in excellent yields irrespective of their position in the aromatic ring (Table 2). Oxindole with a bulky 4-methoxyphenyl substituent at the C5 position provided the desired indoxyl **3o** in good yield. The substrate scope was then evaluated with different Grignard reagents **2**. Apart from phenylmagnesium bromide **2a**, 4-methoxyphenyl-, allyl-, and benzylmagnesium bromides (**2b**, **2c**, and **2d**) furnished the corresponding indoxyls **3v**−**3x**, **3p**−**3u**, and **3y**−**3z**, respectively, in good yields (Table 2). Notably, aliphatic Grignard reagents were found to be less reactive for this transformation. Methylmagnesium bromide **2e** underwent smooth reaction providing the desired indoxyls **3a′**−**3b′** in good yields.

However, the reaction with ethyl, pentyl, 2-ethylhexyl, and cyclohexyl Grignard reagents (**2f**, **2g**, **2h**, and **2i**) were carried out at 70 °C, providing **3c′**, **3d′**, **3e′**, **3f′**, and **3g′** in acceptable yields (Table 2); relatively low yields of the products were obtained at room temperature. Gram-scale experiments using 1 g of **1** were also successful in obtaining the corresponding 2-indoxyls **3** in good yields (Table 2, **3g** and **3r**; Schemes S2 and

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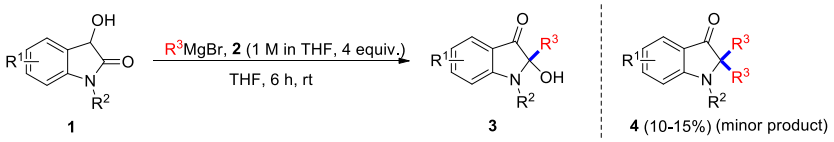
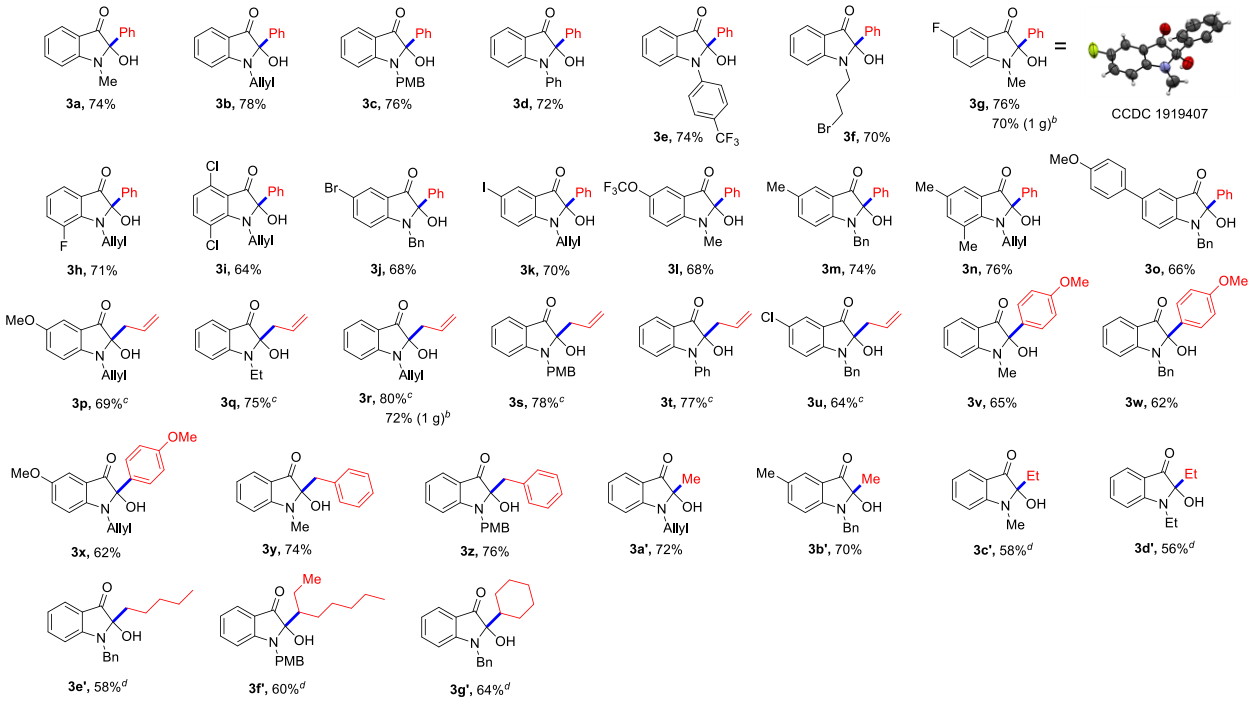
Org. Lett. XXXX, XXX, XXX−XXX

Table 2. Substrate Scope[a]





[a]Reaction conditions: **1** (1.0 mmol), **2** (1 M in THF, 4 equiv), in THF (6 mL) at rt; isolated yields. [b]Reaction performed with 1 g of 3-hydroxyindoline-2-ones **1** for 10 h. [c]Reaction performed with 3 equiv of **2**. [d]Reaction performed at 70 °C.

S3). However, the reaction did not proceed with phenylethynyl and vinyl Grignard reagents.

We propose that the reaction of 3-hydroxy-2-oxindoles **1** initiates with the formation of the intermediate **A**.[22,25,26] The Grignard addition to the intermediate **A** provides the intermediate **B**, which subsequently generates the indolinium ion intermediate **C** (Scheme 2). Then aromatization-driven C3-hydrogen abstraction provides indole intermediate **D**[25b] that tautomerizes by capturing the proton lost during the aromatization to generate indoxyl intermediate **E**. Thus, a 1,2-hydride shift of indolinium ion intermediate **C** generates the indoxyl **E** (Scheme 2). Air-stable indoxyl derivatives like intermediate **E** are reported in the literature.[27] Therefore, aerial oxidation of intermediate **E** takes place under the reaction conditions to provide the desired 2-hydroxyindoxyls **3** as previously reported.[22,26b] We presume that intermediate **E** can suffer ready enolization due to extensive conjugation and exist as indole intermediate **D**. The stability of intermediate **D** may be attributed to the presence of acidic C2-hydrogen and activated carbonyl group, and therefore, no Grignard addition product to the C3-carbonyl group of the intermediate **E** is detected.

Finally, the intermediate **D** undergoes rapid air oxidation during workup to provide 2-hydroxyindoxyls **3** (Scheme 2). This autoxidation pathway presumably initiates with the reaction of the carbanion **F**, generated on workup, with oxygen to form the peroxide intermediate **G** (Scheme 2).[28] Subsequent protonation and elimination of hydroperoxide generates C3-carbonyl indolinium intermediate **I** that undergoes peroxide hydrogen oxidation to give compound **3**.

The formation of the minor product 2,2-disubstituted oxindole **4** could be explained via the intermediate **J**. The Grignard reagent can simultaneously act as a base as well as nucleophile, and thus, it can abstract the acidic C3-hydrogen as well as attack at the C2-center of the indolinium intermediate **C** (Scheme 2). Following workup, the autoxidation of carbanion intermediate **K** produces **4** (Scheme 2). The reaction of carbanion **K** with oxygen produces intermediate **L**, which upon protonation followed by elimination of hydrogen peroxide provides compound **4** (Scheme 2).

To examine whether the oxidation of **D** occurred during or after workup, deuteriated experiments were performed (Scheme 3, a). Quenching the reaction with D_2O following phenylmagnesium bromide **2a** addition to **1c** provided exclusively **3b** without any D incorporation in the final product. If air oxidation of intermediate **D** would have taken place before workup to generate the intermediate **N**, then deuterium labeled product **5** should have been obtained when the reaction was quenched with D_2O (Scheme 3, a). But no such products were observed, which clearly indicates that intermediate **N** does not form under the reaction conditions and the aerial oxidation of intermediate **D** occurs following workup. Furthermore, it was found that addition of radical-trapping reagents TEMPO and galvinoxyl did not inhibit the reaction, indicating that the autoxidation step is an anion-mediated reaction (Scheme 3, b).

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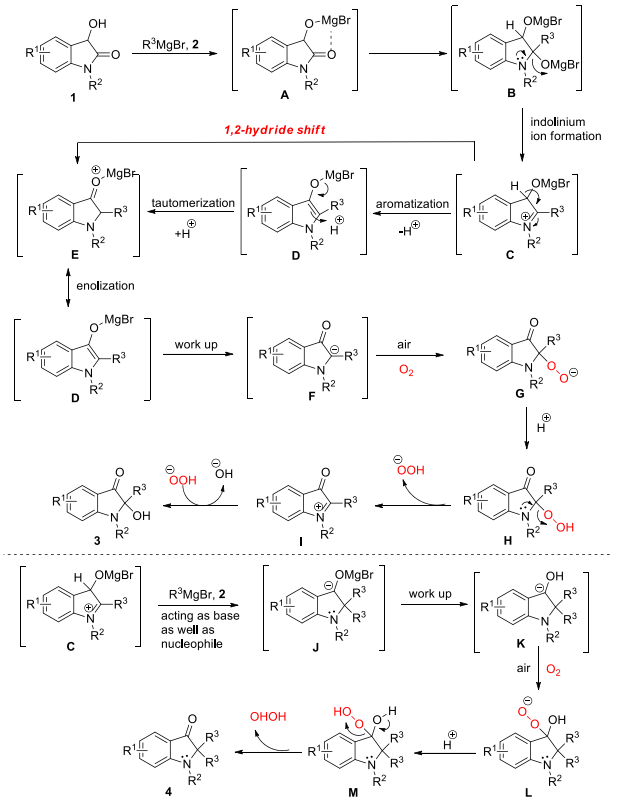
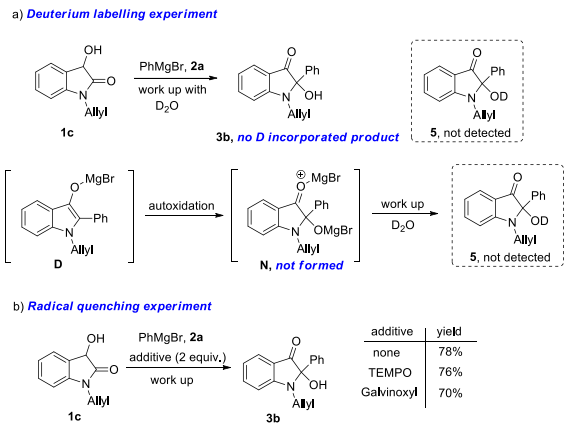
Scheme 2. Probable Mechanism of the Reaction



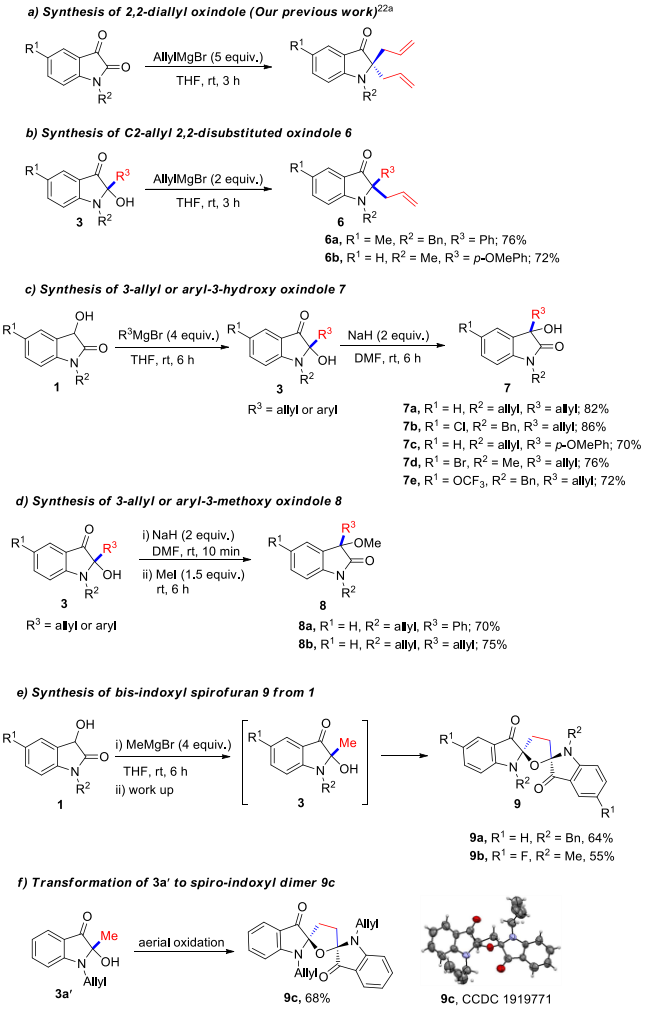
Scheme 3. Control Experiments



We were next intrigued to demonstrate the synthetic potentials of the method by the preparation of functionalized oxindoles. Previously, we have reported the synthesis of 2,2-diallyl-3-oxindoles via Grignard addition of isatins (Scheme 4, a).[25a] In this work, 2,2′-differentially substituted 3-oxindoles **6a,b** containing a C2-allyl group are obtained in good yields via allyl Grignad addition to C2-alkyl or aryl substituted indoxyls **3** that proceeds through a 1,2-allyl shift (Scheme 4, b).

Furthermore, the 2-hydroxyindoxyl derivatives **3** bearing a C2-allyl or aryl group on reaction with sodium hydride provided the corresponding more stable 3-allyl- or aryl-3-hydroxyoxindole derivatives **7a,b** in excellent yields via an *α*-ketol rearrangement (Scheme 4, c).[20,26,29] In addition, sequential treatment of the *N*-protected 3-hydroxy-2-oxindoles **1** with allyl or arylmagnesium bromide followed by the reaction of crude products with sodium hydride provided the

Scheme 4. Synthetic Transformations of 2-Hydroxyindoxyls 3



corresponding oxindole derivatives **7c–e** in good yields (Scheme 4, c; Scheme S6). Moreover, indoxyls **3** upon treatment with sodium hydride followed by methyl iodide afforded the corresponding 3-substituted 3-methoxy derivatives **8a,b** in a one-pot manner (Scheme 4, d).

Interestingly, methylmagnesium bromide addition of **1** provided bis-indoxyl spirofurans **9a,b** via instant aerial oxidation of the in situ generated 2-Me-2-hydroxyindoxyl derivatives **3** (Scheme 4, e).[30] 2-Methyl-2-hydroxyindoxyls **3** were unstable; we could isolate only **3a′** and **3b′** (Table 2). Upon standing, **3a′** was also converted to the spiro-indoxyl dimer **9c** (Scheme 4, f). The structure of **9c** was confirmed by X-ray crystal analysis (Scheme 4, f; CCDC 1919771, Figure S2).

In conclusion, we have developed a one-pot approach to pseudooxindole 2-hydroxyindoxyls by simple Grignard addition to 3-hydroxyoxindoles. The reaction presumably proceeds via 1,2-hydride shift to provide 2-indoxyls, which on autoxidation furnish *N*-substituted 2-hydroxyindoxyls. Notable aspects of this domino nucleophilic addition–oxidation protocol include simple substrates, excellent yield, scalability, broad substrate scope, and operational ease. Moreover, 2-hydroxyindoxyls are effectively used as precursors for the synthesis of 2,2′-differentially substituted 3-oxindoles and a new class of bis-indoxyl spirofurans. We believe that this work

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will provide a new platform to explore the synthetic application of a diverse class of unnatural 2-hydroxyindoxyls and their enantiopure analouges.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b03022.

Experimental procedures, ^{1}H and ^{13}C NMR spectra, and X-ray crystal data (PDF)

Accession Codes

CCDC 1919407 and 1919771 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

Dedicated to Professor Vinod K. Singh on the occasion of his 60th birthday.

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