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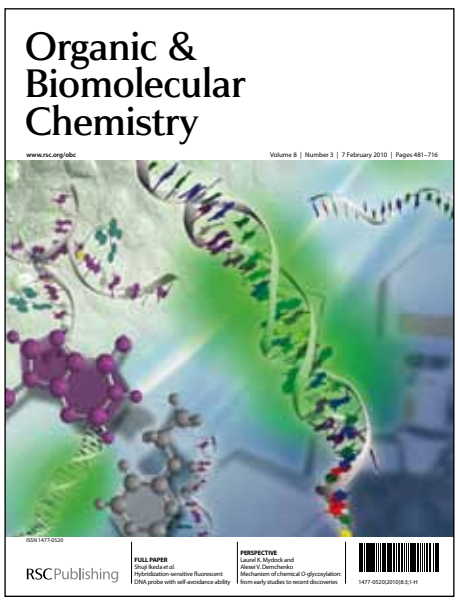

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ARTICLE TYPE

Metal-catalyzed rearrangements of 3-allenyl 3-hydroxyindolin-2-ones in the presence of halogenated reagents

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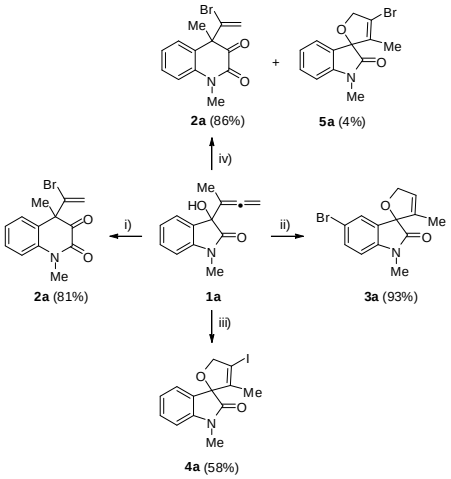
The reactions of 3-allenyl 3-hydroxyoxindoles with a variety of halogenated reagents in the presence of catalytic amounts of precious metal salts were explored. Both, rearrangement and oxycyclization reactions to give 4-(1-halovinyl)-quinolinediones or spirocyclic halooxindoles, respectively, are competitive pathways. The kind of functionalization is substrate and reaction conditions dependent.

Introduction

Transition-metal-catalyzed reactions are among the most powerful tools for the formation of C–C and C–heteroatom bonds.[1] In recent years, developing highly selective catalysts for a single transformation was the main objective. Gold has only been recognized as an active catalyst relatively recently, but catalysis using gold complexes has since blossomed.[2] On the other hand, installing halogens onto bioactive compounds can generate products with novel or improved properties, because halogens often impact the pharmacological profile of a compound.[3] Herein, our efforts focused on harnessing the power of metal salts to catalyze the reactions between 3-allenyl 3-hydroxyoxindoles with a variety of halogenated reagents to effect two different halogenations, namely, rearrangement and oxycyclization reactions to give 4-(1-halovinyl)-quinolinediones or spirocyclic halooxindoles, respectively.

Results and Discussion

As part of our long-standing interest in the synthesis of heterocycles of biological interest,[4] we discovered the ring expansion of 2-azetidinone-tethered allenols to tetramic acids by treatment with brominating reagents.[5] We decide to initiate a related study using 3-allenyl 3-hydroxyindolin-2-ones as substrates.[6] It was found that *N*-bromosuccinimide (NBS) is also a very effective reagent for the ring expansion reaction of allene-derived oxindole **1a** to afford the quinoline-2,3-dione **2a** (Scheme 1). However, to our delight, the addition of a catalytic amount of $AuCl_3$ completely suppressed the rearrangement reaction, giving instead the corresponding spirocyclic 5-bromooxindole **3a** as the sole product (Scheme 1).[7, 8] Thus, it was shown for the first time that it is possible to use a single gold salt for performing two very different and independent transformations, namely, C–O and C–halogen bond formations,[9, 10, 11] in a single reaction sequence. Interestingly, a diphosphine palladium complex in the presence of *N*-iodosuccinimide (NIS) was able to catalyze the iodocycloetherification reaction of allenol **1a** to afford iododihydrofuran **4a** in fair yield, while quinoline-2,3-dione **2a** was achieved by replacing NIS with NBS under otherwise identical conditions, being the bromodihydrofuran **5a** a very minor component.

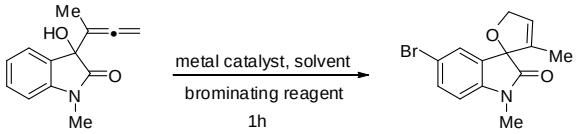


Scheme 1 NXS-initiated divergent preparation of quinoline-2,3-dione **2a**, spirocyclic bromooxindole **3a**, or iodospirocyclic oxindole **4a**. Conditions: (i) NBS, CH_2Cl_2, RT, 1 h. (ii) 5 mol % $AuCl_3$, NBS, CH_2Cl_2, RT, 40 min. (iii) 5 mol % [dppf]$PdCl_2$, NIS, CH_2Cl_2, RT, 6 h. (iv) 5 mol % [dppf]$PdCl_2$, NBS, CH_2Cl_2, RT, 30 min. NBS = N-Bromosuccinimide. NIS = N-Iodosuccinimide. dppf = 1,1'-Bis(diphenylphosphino)ferrocene.

As a consequence, the unexpected gold-catalyzed skeletal reorganization to bromooxindole formation triggered our interest. $AuCl_3$ and AuCl were able to catalyze the formation of bromospirocycle **3a** (Table 1, entries 1 and 2), while iron salts, silver salts, and Brønsted acids were found to be inactive (Table 1, entries 3–5). We employed three different brominating systems in our initial screening for the model system 2-indolinone-tethered allenol **1a**.[12] Initially, the use of NBS was tested. Next, both tribromoisocyanuric acid (TBCA) and bromodimethylsulfonium bromide (BDMS) were investigated;[13] but ring expansion was encountered (Table 1, entries 6 and 7). Apparently, the yields of the bromocycloetherification reaction were improved in dichloromethane. Other solvents, such as tetrahydrofuran and acetonitrile failed to increase the yields

(Table 1, entries 8 and 9).

Table 1 Bromocycloetherification reaction of allenol **1a** under modified metal-catalyzed conditions.

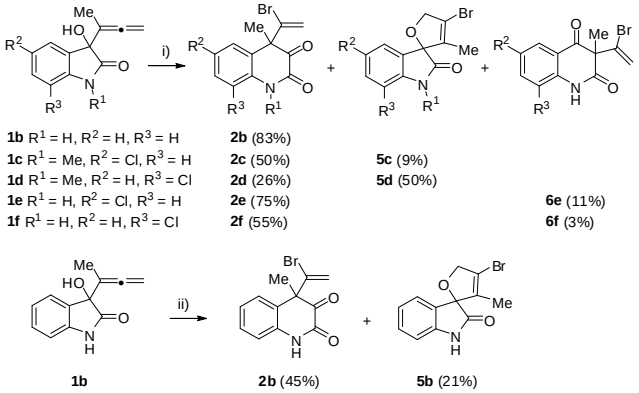


1a **3a**

entry	catalyst (mol %)	reagent [a]	solvent	yield **2a**/**3a** (%)[b]
1	$AuCl_3$ (5)	NBS	CH_2Cl_2	0/93
2	AuCl (5)	NBS	CH_2Cl_2	20/65
3	$FeCl_3$ (5)	NBS	CH_2Cl_2	80/0
4	AgOTf (10)	NBS	CH_2Cl_2	80/0
5	TfOH (10)	NBS	CH_2Cl_2	62/0
6	$AuCl_3$ (5)	TBCA	CH_2Cl_2	55/0[c]
7	$AuCl_3$ (5)	BDMS	CH_2Cl_2	56/0[c]
8	$AuCl_3$ (5)	NBS	THF	0/60
9	$AuCl_3$ (5)	NBS	MeCN	0/63

[a]NBS = N-Bromosuccinimide; TBCA = Tribromoisocyanuric acid; BDMS = Bromodimethylsulfonium bromide. [b]Yield of pure, isolated product with correct analytical and spectral data. [c]The reaction proceeded to completion after 24 h.

Analysis of the spirocycle **3a** showed that the bromine atom becomes attached to the C5 indole carbon. With the optimal conditions in hand, the scope of this reaction was tested with various allenic oxindoles. As revealed in Scheme 2, 1-methyl-3-allenyl 3-hydroxyindolin-2-ones different to **1a** were not suitable for the same transformation, affording quinoline-2,3-diones **2** and spirocyclic bromodihydrofuran derivatives **5** in moderate to good yields. For example, rearrangement adduct **2b** was the sole product from the reaction of the *NH*-derivative **1b** with NBS in presence of $AuCl_3$. The replacement of $AuCl_3$ by $[(MeCN)_2PdCl_2]$ gave as major product **2b** together with a considerable amount of spirocyclic bromodihydrofuran **5b**. The placement of a chlorine atom at C5 and C7 positions of the indole ring were tolerated in presence of $AuCl_3$, providing a handle for subsequent orthogonal reactivity. By contrast with 1-methyl-5-chloro 3-allenyl 3-hydroxyindolin-2-one **1c**, the 7-chloro analogue **1d** afforded as major adduct the spirocyclic bromodihydrofuran derivative **5d**. An interesting case of study are the 5-chloro and 7-chloro *NH*-derivatives **1e** and **1f**, because in absence of $AuCl_3$ the reaction is extremely slow and unselective (quinoline-2,3-dione **2** *versus* quinoline-2,4-dione **6** formation). α-Keto lactam adducts **2e** and **2f**, were selectively obtained in the presence of the gold salt (Scheme 2).



1b R^1 = H, R^2 = H, R^3 = H
1c R^1 = Me, R^2 = Cl, R^3 = H
1d R^1 = Me, R^2 = H, R^3 = Cl
1e R^1 = H, R^2 = Cl, R^3 = H
1f R^1 = H, R^2 = H, R^3 = Cl

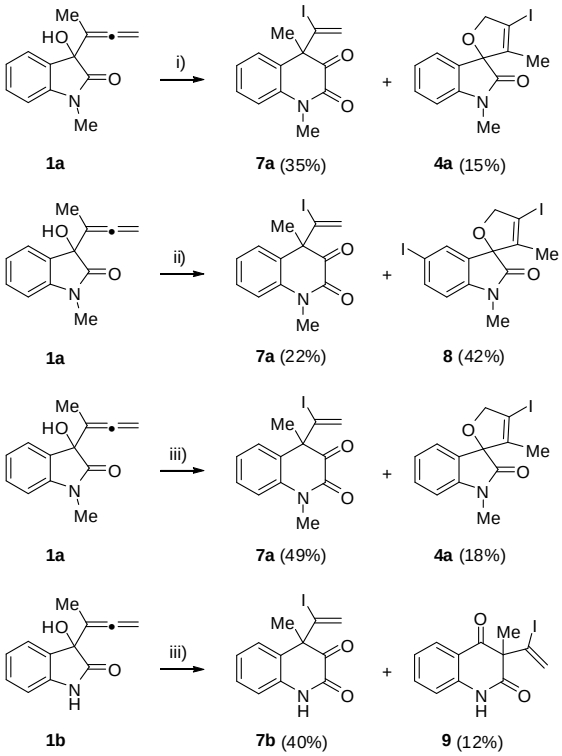
2b (83%) **2c** (50%) **2d** (26%) **2e** (75%) **2f** (55%) **5c** (9%) **5d** (50%) **6e** (11%) **6f** (3%)

1b **2b** (45%) **5b** (21%)

Scheme 2 Preparation of brominated lactams **2**, **5**, and **6** in presence of NBS and $AuCl_3$. Conditions: (i) 5 mol % $AuCl_3$, NBS, CH_2Cl_2, RT, **1b**: 15 min; **1c**: 1 h; **1d**: 1 h; **1e**: 4 h; **1f**: 20 min. (ii) 5 mol % $[(MeCN)_2PdCl_2]$, NBS, CH_2Cl_2, RT, 30 min. NBS = *N*-Bromosuccinimide.

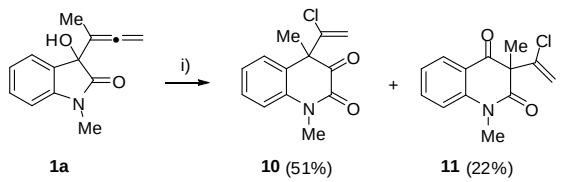
Next, we studied the reaction of allenol **1a** with different iodonium sources such as molecular iodine and bis(pyridine)iodonium tetrafluoroborate (IPy_2BF_4). However, only a small amount of starting material reacted after prolonged reaction times. Fortunately, the combination of I_2 and $PhI(OAc)_2$ is capable of promoting the iodoalkenylation of allene derivative **1a** to afford a separable mixture of quinoline-2,3-dione **7a** and iododihydrofuran **4a** (70:30 ratio) in 50% overall yield in favour of the ring-expanded adduct (Scheme 3). Notably, when $I_2/PhI(OAc)_2/AuCl_3$ was employed by addition of a catalytic amount of $AuCl_3$, decrease of ring expansion reaction was observed, furnishing as the major product the spirocyclic iododihydrofuran **8** with concurrent iodination at the C5 position of the benzenoid ring (Scheme 3). We also examined the reaction of 2-indolinone-tethered allenols **1** with bis(pyridine)iodonium tetrafluoroborate (IPy_2BF_4) in presence of a catalytic amount of $AuCl_3$ (Scheme 3). Starting from **1a**, the only identifiable products from the reaction were the iodinated quinoline-2,3-dione **7a** (major component) and the spirocyclic iododihydrofuran **4a** (minor component). By contrast, the reaction of the *NH*-derivative **1b** with IPy_2BF_4 in presence of $AuCl_3$ proceeds to give the chromatographically separable ring-expanded iodo derivatives **7b** (quinoline-2,3-dione adduct) and **9** (quinoline-2,4-dione adduct).

The quinoline-2,3-dione **2** *versus* quinoline-2,4-dione **6** formation is related to the migration of the carbonyl group (adduct **6**), or the migration of aryl group (adduct **2**), during ring expansion. Quinoline-2,4-dione **6** are always very minor products with respect to adducts **2**, which is due to a facilitated migrating behavior of the aryl group. On the other hand, from results in Scheme 2 and Scheme 3 it may be inferred that *NH*-indolones exclusively suffer ring expansion, while the formation of quinolinediones from *N*-methyl indolones is always accompanied by spirocyclic products. Thus, *N*-unsubstituted indolones **1** are more prone to suffer rearrangement because the ring opening of NH-indolones is normally easier than the cleavage of N-methyl indolones.



Scheme 3 Preparation of iodinated lactams **4**, **7**, **8**, and **9** in presence of I_2, $PhI(OAc)_2$, IPy_2BF_4 and $AuCl_3$. Conditions: (i) I_2, $PhI(OAc)_2$, CH_2Cl_2, RT, 12 h. (ii) 5 mol % $AuCl_3$, I_2, $PhI(OAc)_2$, CH_2Cl_2, RT, 1 h. (iii) 5 mol % $AuCl_3$, IPy_2BF_4, CH_2Cl_2, RT, **1a**: 1 h; **1b**: 4 h.

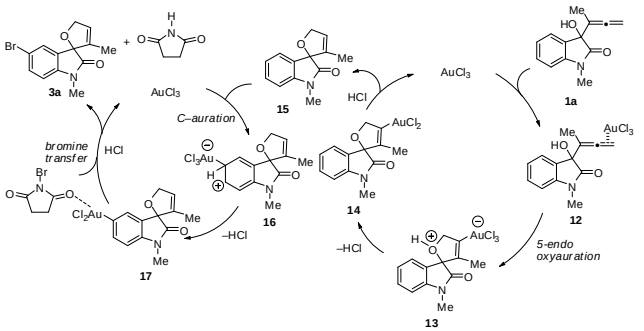
Then we decided to adapt our protocol for the synthesis of chloro-substituted derivatives. We chose the reaction between 2-indolinone-tethered allenol **1a** and *N*-chlorosuccinimide (NCS) in presence of a catalytic amount of $AuCl_3$ as a model. Unfortunately, analysis of the mixture revealed a complicated reaction leading to non-identifiable products. Next, we identified silver catalysis as a potential catalytic source, since silver salts have demonstrated its effectiveness in the activation of carbon–carbon multiple bonds.[14] The use of silver salts such as AgOTf or $AgNO_3$ led to mixtures of products, in which quinolinediones were detected in low yield. Interestingly, the treatment of allenol **1a** with a catalityc amount (10 mol%) of the less electrophilic silver precatalyst [Ag(phen)OTf],[15] in acetonitrile at 75°C for 20 h produces the chromatographically separable ring-expanded chloro derivative **10** (quinoline-2,3-dione adduct) as a major product, along with its quinoline-2,4-dione counterpart **11** in a 73% overall yield (Scheme 4).



Scheme 4 Preparation of chlorinated lactams **10** and **11** in presence of NCS and [Ag(phen)OTf]. Conditions: (i) 10 mol % [Ag(phen)OTf], NCS, MeCN, 75°C, 20 h. NCS = *N*-chlorosuccinimide.

An attempt to improve the efficiency of the formation of **10** by increasing the reaction temperature to 140°C met with failure, because despite the [Ag(phen)OTf]-catalyzed reaction of allenol **1a** with NCS proceeded in 9 h, it resulted in the formation of the quinolines **10** and **11** in a moderate yield of 60%.

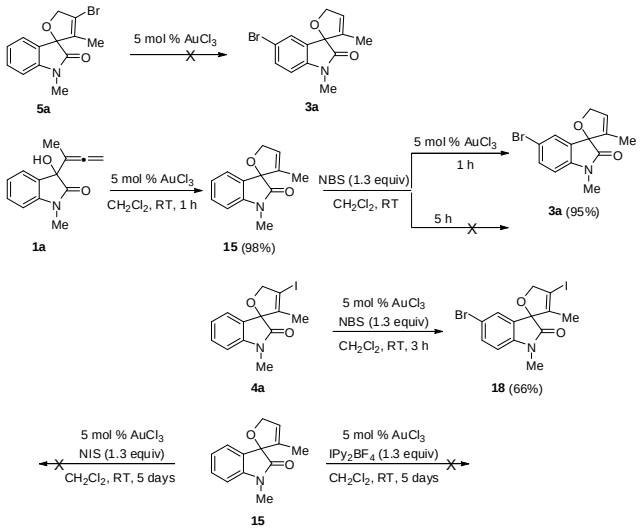
Mechanistically, the gold-catalyzed achievement of spirocyclic bromooxindole **3a** might proceed in a tandem sequence involving as first step the formation of complex **12** through coordination of gold trichloride to the distal allenic double bond of α-allenol **1a**. Next, regioselective 5-*endo* oxyauration[16] forms zwitterionic intermediate **13**, which after loss of HCl generate neutral species **14**. Protonolysis of the carbon–gold bond of **14** liberates adduct **15**, releasing the gold catalyst into the first catalytic cycle (Scheme 5). Next, spirocyclic oxindole **15** enter the second catalytic cycle, which is also gold-catalyzed,[17] generating zwitterionic species **16** by formation of a C–Au bond in an electrophilic substitution fashion.[18] Subsequent loss of HCl would regenerate the aromatic ring and would form the neutral arylgold(III) species **17**. *N*-Bromosuccinimide is then activated by the gold complex. Demetalation linked to bromine transfer in the presence of NBS liberate bromoadduct **3a** and succinimide with concomitant regeneration of the gold catalyst, closing the second catalytic cycle (Scheme 5).



Scheme 5 Mechanistic explanation for the Au(III)-catalyzed arene bromination/spirocyclization reaction sequence of 3-allenyl 3-hydroxyindolin-2-one **1a**.

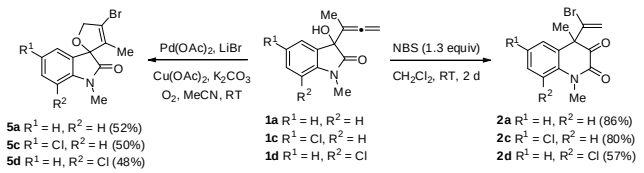
In order to see if compound **5a** is able to rearrange to **3a** under metal catalysis, reaction of **5a** with a catalytic amount of $AuCl_3$ was conducted in the absence of NBS. The reaction did not proceed (Scheme 6). In contrast, reaction of **15** with a catalytic amount of $AuCl_3$ and NBS gave the brominated product **3a** (Scheme 6). We performed the spirocyclization of allenol **1a** and its reaction with NBS (in presence of $AuCl_3$ or not). Under otherwise the same conditions, but without the addition of NBS, cycloetherification reaction of 3-allenyl 3-hydroxyindolin-2-one **1a** catalyzed by $AuCl_3$ in dichloromethane afforded spirocyclic dihydrofuran **15** in almost quantitative yield (Scheme 6). Adduct **15** was treated with NBS both in presence or absence of $AuCl_3$. After five hours, compound **15** was unreactive in the absence of the gold salt. By contrast, the reaction of allenol **1a** with NBS catalyzed by $AuCl_3$ was very fast, affording bromospirocycle **3a** in 95% yield (Scheme 6). The fact that the $AuCl_3$-catalyzed conversion of adduct **15** in the presence of NBS afforded bromoadduct **3a**, suggests the decisive role of the gold salt in promoting the halogenation of the aromatic ring. Similarly, iododihydrofuran **4a** can be brominated at the benzene ring with NBS under gold catalysis (Scheme 6). In contraposition to

bromination, the $AuCl_3$-catalyzed reaction of adduct **15** in the presence of NIS or (IPy_2BF_4) did not proceed (Scheme 6).



Scheme 6 Reactions of adducts **15** and **4a** in presence of NBS and $AuCl_3$ to give bromoadducts **3a** and **18**.

With the aim of increasing selectivity, several modifications were attempted. Controlled ring-expansion reactions of 3-allenyl 3-hydroxyindolin-2-ones **1a**, **1c**, and **1d** to efficiently afford quinoline-2,3-diones **2a**, **2c**, and **2d** as sole products, have been achieved trough controlled C–C bond cleavage of the gamma-lactam nucleus by reaction with NBS in the absence of any metal salt (Scheme 7). Besides, bromodihydrofurans **5a**, **5c**, and **5d** were exclusively obtained using LiBr as the halogenating reagent in the presence of $Pd(OAc)_2$, $Cu(OAc)_2$ and K_2CO_3 under an atmospheric pressure of oxygen (Scheme 7). Therefore, selective conditions for the preparation both of ring expansion and spirocycle adducts have been found.



Scheme 7 Selective divergent preparation of quinoline-2,3-diones **2** and bromodihydrofurans **3** from 3-allenyl 3-hydroxyindolin-2-ones **1** under modified halogenation conditions.

Conclusions

In conclusion, the reactions of 3-allenyl 3-hydroxyoxindoles with a variety of halogenated reagents in the presence of catalytic amounts of precious metal salts were explored. Both, rearrangement and oxycyclization reactions to give 4-(1-halovinyl)-quinolinediones or spirocyclic halooxindoles, respectively, are competitive pathways. The kind of functionalization is substrate and reaction conditions dependent: $AuCl_3$ in the presence of NBS afforded as major adducts quinoline-2,3-diones, $AuCl_3$ in the presence of I_2/$PhI(OAc)_2$ favors the formation of spirocyclic iododihydrofurans, whereas $AuCl_3$ in the presence of IPy_2BF_4 enterely gives ring expansion adducts. Besides, it has been observed that the reaction with NCS catalyzed by [Ag(phen)OTf] exclusively produces the ring-expanded chloro derivatives. By contrast, the Pd-catalyzed reaction with BrLi gave spirocyclic bromodihydrofurans as the sole products.

Experimental section

^1H NMR and ^{13}C NMR spectra were recorded on 700 or 300 MHz spectrometers. NMR spectra were recorded in $CDCl_3$ solutions, except otherwise stated. Chemical shifts are given in ppm relative to TMS (^1H, 0.0 ppm), or $CDCl_3$ (^{13}C, 76.9 ppm). Low and high resolution mass spectra were taken on a QTOF LC/MS spectrometer using the electronic impact (EI) or electrospray modes (ES) unless otherwise stated. All commercially available compounds were used without further purification.

Indium-promoted reaction between 3-substituted prop-2-ynyl bromides and isatins; general procedure for the synthesis of α-allenic alcohols 1a–f. 1-Bromo-2-butyne (3.0 mmol) was added to a well stirred suspension of the corresponding isatin (1.0 mmol) and indium powder (6.0 mmol) in THF/NH_4Cl (aq. sat.) (1:5, 5 mL) at 0 °C. After disappearance of the starting material (TLC) the mixture was extracted with ethyl acetate (3 x 5 mL). The organic extract was washed with brine, dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using ethyl acetate/hexanes or dichloromethane/ethyl acetate mixtures gave analytically pure compounds. Spectroscopic and analytical data for previously unreported α-allenic alcohols **1** follow.

α-Allenic Alcohol 1c. From 100 mg (0.50 mmol) of *N*-methyl 5-chloroisatin, and after chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent gave compound **1c** (106 mg, 90%) as a colorless solid; mp 160–162 ºC; ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.23 (m, 2H), 6.70 (d, *J* = 7.8 Hz, 1H), 5.00 (q, *J* = 3.0 Hz, 2H), 3.12 (s, 3H), 1.47 (t, *J* = 3.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 204.7, 176.2, 142.4, 130.7, 129.9, 128.7, 125.1, 109.4, 100.4, 80.9, 76.2, 26.5, 13.7; IR ($CHCl_3$): ν = 3365, 2990, 1944, 1714 cm^{-1}; HRMS (ES): calcd for $C_{13}H_{13}ClNO_2$ [*M* + H]$^+$: 250.0635; found: 250.0632.

α-Allenic Alcohol 1d. From 100 mg (0.50 mmol) of *N*-methyl 7-chloroisatin, and after chromatography of the residue using hexanes/ethyl acetate (3:1) as eluent gave compound **1d** (98 mg, 83%) as a colorless solid; mp 130–132 ºC; ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.29 (m, 2H), 6.92 (t, *J* = 7.8 Hz, 1H), 4.94 (q, *J* = 3.0 Hz, 2H), 3.48 (s, 3H), 1.48 (t, *J* = 3.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 204.9, 177.1, 139.6, 132.2, 132.1, 124.0, 123.1, 115.9, 100.6, 80.5, 75.8, 29.8, 13.7; IR ($CHCl_3$): ν = 3380, 2986, 1946, 1714 cm^{-1}; HRMS (ES): calcd for $C_{13}H_{13}ClNO_2$ [*M* + H]$^+$: 250.0635; found: 250.0636.

α-Allenic Alcohol 1e. From 272 mg (1.50 mmol) of 5-chloroisatin, and after chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent gave compound **1e** (220 mg, 63%) as a colorless solid; mp 206–208 ºC; ^1H NMR (300 MHz, acetone-d_6, 25 °C): δ = 9.44 (br s, 1H), 7.27 (m, 2H), 6.92 (d, *J* =

8.2 Hz, 1H), 4.77 (m, 2H), 1.76 (t, J = 3.1 Hz, 3H); ^{13}C NMR (75 MHz, acetone-d_6, 25 °C): δ = 206.9, 177.9, 141.5, 134.3, 130.0, 127.5, 125.9, 112.0, 101.2, 78.3, 77.3, 13.8; IR ($CHCl_3$): ν = 3326, 2923, 1945, 1724 cm^{-1}; HRMS (ES): calcd for $C_{12}H_9ClNO$ [(M + H) – H_2O]$^+$: 218.0373; found: 218.0378.

α-Allenic Alcohol 1f. From 181 mg (1.0 mmol) of 7-chloroisatin, and after chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent gave compound **1f** (155 mg, 65%) as a a yellow solid; mp 157–159 °C; ^{1}H NMR (300 MHz, acetone-d_6, 25 °C): δ = 9.61 (br s, 1H), 7.28 (m, 2H), 7.04 (t, J = 7.8 Hz, 1H), 4.74 (m, 2H), 1.76 (t, J = 3.1 Hz, 3H); ^{13}C NMR (75 MHz, acetone-d_6, 25 °C): δ = 206.9, 177.8, 140.4, 134.2, 130.1, 124.3, 124.1, 115.3, 101.2, 78.2, 77.9, 13.9; IR ($CHCl_3$): ν = 3229, 2925, 1941, 1724 cm^{-1}; HRMS (ES): calcd for $C_{12}H_9ClNO$ [(M + H) – H_2O]$^+$: 218.0373; found: 218.0377.

General Procedure for the Reaction of 3-Allenyl 3-Hydroxyindolin-2-ones 1 with NBS or NIS in the Presence of Pd(II). To a solution of the corresponding indolin-2-one-tethered allenol **1** (0.50 mmol) and the appropriate palladium salt (0.025 mmol) in dichloromethane (20 mL) was added *N*-bromosuccinimide or *N*-iodosuccinimide (1.3 equiv). The reaction mixture was stirred at RT until the starting material disappeared as indicated by TLC. Saturated aqueous sodium hydrogen carbonate (5 mL) was added, before being partitioned between dichloromethane and water. The organic extract was washed with brine, dried ($MgSO_4$), concentrated under vacuum, and purified by flash column chromatography eluting with ethyl acetate/hexanes or dichloromethane/ethyl acetate mixtures. Spectroscopic and analytical data for pure forms of compounds **2**, **4**, and **5** follow.

Spirocyclic Iododihydrofuran 4a. From 30 mg (0.14 mmol) of indolin-2-one-tethered allenol **1a**, and after chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent gave compound **4a** (27 mg, 58%) as a colorless solid; mp 105–107 °C; ^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C) δ: 7.35 (td, J = 7.6, 1.4 Hz, 1H), 7.20 (d, J = 7.5 Hz, 1H), 7.08 (td, J = 7.6, 0.8 Hz, 1H), 6.83 (d, J = 7.8 Hz, 1H), 5.00 and 4.89 (dq, J = 11.7, 2.0 Hz, each 1H), 3.20 (s, 3H), 1.45 (t, J = 2.0 Hz, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$, 25 °C) δ: 174.3, 143.8, 139.3, 130.5, 127.3, 124.6, 123.3, 108.4, 91.9, 88.6, 82.5, 26.3, 13.0; IR ($CHCl_3$, cm^{-1}): ν 1701; HRMS (ES): calcd for $C_{13}H_{13}INO_2$[M + H]$^+$: 341.9991; found: 341.9996.

Reaction between Allenol 1a and *N*-Bromosuccinimide in the Presence of [dppf]PdCl$_2$. Preparation of Quinoline-2,3-dione 2a and Spirocyclic Bromodihydrofuran 5a. From 90 mg (0.42 mmol) of indolin-2-one-tethered allenol **1a**, and after chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent, 5 mg (4%) of the less polar compound **5a** and 108 mg (86%) of the more polar compound **2a** were obtained.

Quinoline-2,3-dione 2a. Colorless solid; mp 93–95 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ: 7.36 (m, 4H), 5.85 and 5.82 (d, J = 3.2 Hz, each 1H), 3.41 (s, 3H), 1.67 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ: 190.9, 155.0, 137.1, 131.7, 129.6, 127.4, 126.1, 124.4, 121.6, 116.5, 60.4, 30.0, 21.9; IR ($CHCl_3$, cm^{-1}): ν 1743, 1684; HRMS (ES): calcd for $C_{13}H_{13}BrNO_2$ [M + H]$^+$: 294.0130; found: 294.0123.

Spirocyclic Bromodihydrofuran 5a. Colorless solid; mp 230–231 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ: 7.36 (td, J = 7.7, 1.5 Hz, 1H), 7.24 (ddd, J = 7.3, 1.5, 0.5 Hz, 1H), 7.10 (td, J = 7.4, 1.0 Hz, 1H), 6.85 (d, J = 7.8 Hz, 1H), 5.15 and 5.05 (dq, J = 11.5, 2.0 Hz, each 1H), 3.22 (s, 3H), 1.41 (t, J = 2.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ: 174.3, 143.9, 132.8, 130.6, 130.5, 127.2, 124.6, 123.3, 108.5, 92.3, 78.7, 26.3, 10.4; IR ($CHCl_3$, cm^{-1}): ν 1708; HRMS (ES): calcd for $C_{13}H_{13}BrNO_2$ [M + H]$^+$: 294.0130; found: 294.0130.

Reaction between Allenol 1b and *N*-Bromosuccinimide in the Presence of [(MeCN)$_2$PdCl$_2$]. Preparation of Quinoline-2,3-dione 2b and Spirocyclic Bromodihydrofuran 5b. From 25 mg (0.12 mmol) of indolin-2-one-tethered allenol **1b**, and after chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent, 7 mg (21%) of the less polar compound **5b** and 15 mg (45%) of the more polar compound **2b** were obtained.

Quinoline-2,3-dione 2b. Colorless solid; mp 178–180 °C; ^{1}H NMR (300 MHz, DMSO-d_6, 25 °C) δ: 11.45 (br s, 1H), 7.30 and 7.10 (m, each 2H), 6.01 and 5.87 (d, J = 3.2 Hz, each 1H), 1.64 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ: 192.5, 154.0, 134.9, 132.1, 129.3, 127.6, 126.1, 123.8, 120.9, 116.6, 61.0, 23.8; IR ($CHCl_3$, cm^{-1}): ν 3230, 1738, 1695, 1372; HRMS (ES): calcd for $C_{12}H_{11}BrNO_2$ [M + H]$^+$: 279.9973; found: 279.9969.

Spirocyclic Bromodihydrofuran 5b. Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ: 7.89 (br, 1H), 7.31 (t, J = 6.7 Hz, 1H), 7.21 (d, J = 6.7 Hz, 1H), 7.07 (t, J = 7.5 Hz, 1H), 6.88 (d, J = 7.8 Hz, 1H), 5.01 and 4.88 (m, 1H), 1.49 (t, J = 2.0 Hz, 3H); IR ($CHCl_3$, cm^{-1}): ν 3342, 1712; HRMS (ES): calcd for $C_{12}H_{11}BrNO_2$ [M + H]$^+$: 279.9973; found: 279.9973.

General Procedure for the Reaction of 3-Allenyl 3-Hydroxyindolin-2-ones 1 with NBS in the Presence of Au(III). A solution of the gold salt (0.025 mmol) and *N*-bromosuccinimide (1.3 equiv) in dichloromethane (10 mL) was stirred for five minutes. Then, a solution of the corresponding indolin-2-one-tethered allenol **1** (0.50 mmol) in dichloromethane (10 mL) was added. The reaction mixture was stirred at RT until the starting material disappeared as indicated by TLC. Saturated aqueous sodium hydrogen carbonate (5 mL) was added, before being partitioned between dichloromethane and water. The organic extract was washed with brine, dried ($MgSO_4$), concentrated under vacuum, and purified by flash column chromatography eluting with ethyl acetate/hexanes or dichloromethane/ethyl acetate mixtures. Spectroscopic and analytical data for pure forms of compounds **2**, **3**, **5**, and **6** follow.

Spirocyclic 5-Bromooxindole 3a. From 30 mg (0.14 mmol) of indolin-2-one-tethered allenol **1a**, and after chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent gave compound **3a** (37 mg, 93%) as a colorless oil; ^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C) δ: 7.45 (dd, J = 8.3, 2.0 Hz, 1H), 7.31 (s, 1H), 6.70 (d, J = 8.3 Hz, 1H), 5.97 (q, J = 1.5 Hz, 1H), 5.00 and

4.90 (dt, J = 12.4, 2.0 Hz, each 1H), 3.18 (s, 3H), 1.43 (t, J = 2.0 Hz, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$, 25 °C) δ: 175.1, 143.1, 135.3, 132.9, 130.4, 127.8, 125.4, 115.9, 109.9, 92.3, 76.7, 26.5, 11.2; IR ($CHCl_3$, cm^{-1}): ν 1705; HRMS (ES): calcd for $C_{13}H_{13}BrNO_2[M + H]^+$: 294.0130; found: 294.0135.

Quinoline-2,3-dione 2b. From 25 mg (0.12 mmol) of indolin-2-one-tethered allenol **1b**, and after chromatography of the residue using hexanes/ethyl acetate (5:2) as eluent gave compound **2b** (27 mg, 83%) as a colorless solid; mp 178–180 °C.

Reaction between Allenol 1c and *N*-Bromosuccinimide in the Presence of $AuCl_3$. Preparation of Quinoline-2,3-dione 2c and Spirocyclic Bromodihydrofuran 5c. From 25 mg (0.10 mmol) of indolin-2-one-tethered allenol **1c**, and after chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent, 3 mg (9%) of the less polar compound **5c** and 16 mg (50%) of the more polar compound **2c** were obtained.

Quinoline-2,3-dione 2c. Pale brown solid; mp 145–147 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ: 7.38 (dd, J = 8.8, 2.4 Hz, 1H), 7.31 (d, J = 2.4 Hz, 1H), 7.05 (d, J = 8.8 Hz, 1H), 5.83 and 5.74 (d, J = 3.0 Hz, each 1H), 3.48 (s, 3H), 1.73 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ: 189.9, 155.7, 136.1, 131.2, 130.1, 129.7, 128.4, 127.8, 121.5, 117.1, 60.6, 30.4, 21.4; IR ($CHCl_3$, cm^{-1}): ν 1743, 1686, 1492, 1360; HRMS (ES): calcd for $C_{13}H_{12}BrClNO_2$ $[M + H]^+$: 327.9740; found: 327.9738.

Spirocyclic Bromodihydrofuran 5c. Pale brown oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ: 7.26 (dd, J = 8.1, 2.1 Hz, 1H), 7.13 (d, J = 2.1 Hz, 1H), 6.70 (d, J = 8.4 Hz, 1H), 4.95 and 4.80 (dq, J = 11.7, 2.1 Hz, each 1H), 3.11 (s, 3H), 1.36 (t, J = 2.1 Hz, 3H); IR ($CHCl_3$, cm^{-1}): ν 1706; HRMS (ES): calcd for $C_{13}H_{12}BrClNO_2$ $[M + H]^+$: 327.9740; found: 327.9724.

Reaction between Allenol 1d and *N*-Bromosuccinimide in the Presence of $AuCl_3$. Preparation of Quinoline-2,3-dione 2d and Spirocyclic Bromodihydrofuran 5d. From 27 mg (0.11 mmol) of indolin-2-one-tethered allenol **1d**, and after chromatography of the residue using hexanes/ethyl acetate (4:1) as eluent, 16 mg (50%) of the less polar compound **5d** and 10 mg (26%) of the more polar compound **2d** were obtained.

Quinoline-2,3-dione 2d. Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ: 7.48 (dd, J = 7.8, 1.8 Hz, 1H), 7.26 (m, 2H), 5.77 and 5.59 (d, J = 2.9 Hz, each 1H), 3.50 (s, 3H), 1.73 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ: 191.2, 160.1, 136.7, 132.6, 132.2, 130.8, 126.6, 125.9, 125.6, 120.8, 60.6, 36.3, 18.5; IR ($CHCl_3$, cm^{-1}): ν 1734, 1609, 1461, 1112 cm^{-1}; HRMS (ES): calcd for $C_{13}H_{12}BrClNO_2$ $[M + H]^+$: 327.9740; found: 327.9742.

Spirocyclic Bromodihydrofuran 5d. Pale brown oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ: 7.27 (dd, J = 7.6, 1.3 Hz, 1H), 7.10 (dd, J = 7.3, 1.3 Hz, 1H), 7.00 (t, J = 7.3 Hz, 1H), 5.01 and 4.86 (dq, J = 11.7, 2.0 Hz, each 1H), 3.56 (s, 3H), 1.43 (t, J = 2.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ: 174.6, 139.7, 132.8, 132.6, 130.1, 124.1, 123.3, 115.9, 115.4, 91.6, 78.8, 29.8, 10.4; IR ($CHCl_3$, cm^{-1}): ν 1706; HRMS (ES): calcd for $C_{13}H_{12}BrClNO_2$ $[M + H]^+$: 327.9740; found: 327.9734.

Reaction between Allenol 1e and *N*-Bromosuccinimide in the Presence of $AuCl_3$. Preparation of Quinoline-2,3-dione 2e and Quinoline-2,4-dione 6e. From 30 mg (0.13 mmol) of indolin-2-one-tethered allenol **1e**, and after chromatography of the residue using hexanes/ethyl acetate (3:1) as eluent, 5 mg (11%) of the less polar compound **6e** and 31 mg (75%) of the more polar compound **2e** were obtained.

Quinoline-2,3-dione 2e. Yellow solid; mp 235–237 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ: 9.73 (br s, 1H), 7.30 (m, 2H), 6.98 (d, J = 8.5 Hz, 1H), 5.94 and 5.92 (d, J = 3.0 Hz, each 1H), 1.73 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ: 190.4, 154.8, 132.1, 130.6, 130.3, 129.7, 128.0, 127.9, 121.5, 118.3, 61.5, 23.6; IR ($CHCl_3$, cm^{-1}): ν 3245, 1698, 1492, 1368 cm^{-1}; HRMS (ES): calcd for $C_{12}H_{10}BrClNO_2$ $[M + H]^+$: 313.9583; found: 313.9585.

Quinoline-2,4-dione 6e. Yellow solid; mp 167–169 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ: 9.62 (br s, 1H), 7.96 (d, J = 2.5 Hz, 1H), 7.55 (dd, J = 8.6, 2.5 Hz, 1H), 7.03 (d, J = 8.6 Hz, 1H), 6.12 and 5.96 (d, J = 3.2 Hz, each 1H), 1.72 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ: 192.0, 171.9, 138.9, 136.4, 129.6, 127.8, 127.4, 121.4, 119.2, 118.1, 65.1, 22.9; IR ($CHCl_3$, cm^{-1}): ν 3248, 1705, 1670, 1485, 1370 cm^{-1}; HRMS (ES): calcd for $C_{12}H_{10}BrClNO_2$ $[M + H]^+$: 313.9583; found: 313.9590.

Reaction between Allenol 1f and *N*-Bromosuccinimide in the Presence of $AuCl_3$. Preparation of Quinoline-2,3-dione 2f and Quinoline-2,4-dione 6f. From 30 mg (0.13 mmol) of indolin-2-one-tethered allenol **1e**, and after chromatography of the residue using dichloromethane as eluent, 1 mg (3%) of the less polar compound **6f** and 22 mg (52%) of the more polar compound **2f** were obtained.

Quinoline-2,3-dione 2f. Yellow solid; mp 103–105 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ: 8.55 (br s, 1H), 7.43 (dd, J = 8.0, 1.0 Hz, 1H), 7.23 (dd, J = 8.0, 1.5 Hz, 1H), 7.13 (t, J = 8.0 Hz, 1H), 5.92 (dd, J = 4.3, 3.0 Hz, 2H), 1.73 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ: 190.2, 153.6, 130.8, 130.5, 129.6, 127.9, 126.5, 124.9, 121.5, 120.6, 61.6, 23.5; IR ($CHCl_3$, cm^{-1}): ν 3242, 1698, 1484, 1347 cm^{-1}; HRMS (ES): calcd for $C_{12}H_{10}BrClNO_2$ $[M + H]^+$: 313.9583; found: 313.9583.

(Quinoline-2,4-dione 6f. Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ: 8.24 (br s, 1H), 7.95 (d, J = 8.0 Hz, 1H), 7.66 (d, J = 8.0 Hz, 1H), 7.15 (t, J = 8.0 Hz, 1H), 6.10 and 5.95 (d, J = 3.0 Hz, each 1H), 1.72 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ: 192.3, 169.9, 137.1, 136.2, 127.3, 127.2, 123.9, 121.5, 120.1, 119.5, 65.3, 22.8; IR ($CHCl_3$, cm^{-1}): ν 3250, 1702, 1668, 1480, 1372 cm^{-1}; HRMS (ES): calcd for $C_{12}H_{10}BrClNO_2$ $[M + H]^+$: 313.9583; found: 313.9576.

General Procedure for the Reaction of 3-Allenyl 3-Hydroxyindolin-2-ones 1 with I_2/PhI(OAc)$_2$. PhI(OAc)$_2$ (1.50 mmol) and I_2 (1.50 mmol) were sequentially added to a solution of the corresponding indolin-2-one-tethered allenol **1** (0.50

mmol) in dichloromethane (10 mL). The reaction mixture was stirred at RT until the starting material disappeared as indicated by TLC. Saturated aqueous sodium thiosulfate (5 mL) was added, before being partitioned between dichloromethane and water. The organic extract was washed with brine, dried ($MgSO_4$), concentrated under vacuum, and purified by flash column chromatography eluting with ethyl acetate/hexanes or dichloromethane/ethyl acetate mixtures. Spectroscopic and analytical data for pure forms of compounds **7** and **4** follow.

Preparation of Quinoline-2,3-dione 7a and Spirocyclic Iododihydrofuran 4a. From 30 mg (0.14 mmol) of indolin-2-one-tethered allenol **1a**, and after chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent, 7 mg (15%) of the less polar compound **4a** and 16 mg (35%) of the more polar compound **7a** were obtained.

Quinoline-2,3-dione 7a. Yellow solid; mp 140–142 ºC; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C) δ: 7.45 (td, *J* = 8.2, 1.6 Hz, 1H), 7.34 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.22 (td, *J* = 7.5, 1.0 Hz, 1H), 7.11 (dd, *J* = 8.2, 0.7 Hz, 1H), 6.15 and 6.13 (d, *J* = 2.8 Hz, each 1H), 3.48 (s, 3H), 1.70 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C) δ: 191.0, 156.5, 137.6, 130.0, 129.8, 127.8, 127.5, 124.6, 115.8, 110.2, 61.9, 30.1, 21.3; IR ($CHCl_3$, cm^{-1}): ν 1741, 1682; HRMS (ES): calcd for $C_{13}H_{13}INO_2$ [*M* + H]$^+$: 341.9991; found: 341.9999.

General Procedure for the Reaction of 3-Allenyl 3-Hydroxyindolin-2-ones 1 with I_2/PhI(OAc)$_2$ in the Presence of $AuCl_3$. The corresponding indolin-2-one-tethered allenol **1** (0.50 mmol) was added to a solution of PhI(OAc)$_2$ (1.50 mmol), I_2 (1.50 mmol), and $AuCl_3$ (0.025 mmol) in dichloromethane (10 mL). The reaction mixture was stirred at RT until the starting material disappeared as indicated by TLC. Saturated aqueous sodium thiosulfate (5 mL) was added, before being partitioned between dichloromethane and water. The organic extract was washed with brine, dried ($MgSO_4$), concentrated under vacuum, and purified by flash column chromatography eluting with ethyl acetate/hexanes or dichloromethane/ethyl acetate mixtures. Spectroscopic and analytical data for pure forms of compounds **8** follow.

Preparation of Quinoline-2,3-dione 7a and Diiodinated spirocycle 8. From 40 mg (0.18 mmol) of indolin-2-one-tethered allenol **1a**, and after chromatography of the residue using hexanes/ethyl acetate (5:1) as eluent, 35 mg (42%) of the less polar compound **8** and 13 mg (22%) of the more polar compound **7a** were obtained.

Diiodinated Spirocycle 8. Colorless solid; mp 162–164 ºC; ^{1}H-NMR (300 MHz, $CDCl_3$, 25 ^{o}C) δ: 7.66 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.46 (d, *J* = 1.5 Hz, 1H), 6.62 (d, *J* = 8.2 Hz, 1H), 4.98 and 4.86 (dq, *J* = 11.7, 2.0 Hz, each 1H), 3.17 (s, 3H), 1.46 (t, *J* = 2.0 Hz, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$, 25 ^{o}C) δ: 173.5, 143.5, 139.3, 138.7, 133.3, 129.6, 110.5, 91.5, 89.2, 85.7, 82.7, 26.4, 13.0; IR ($CHCl_3$, cm^{-1}): ν 1727; HRMS (ES): calcd for $C_{13}H_{12}I_2NO_2$[*M* + H]$^+$: 467.8957; found: 467.8967.

Reaction between Allenol 1a and IPy_2BF_4 in the Presence of $AuCl_3$. Preparation of Quinoline-2,3-dione 7a and Spirocyclic Iododihydrofuran 4a. From 30 mg (0.14 mmol) of indolin-2-one-tethered allenol **1a**, and after chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent, 8 mg (17%) of the less polar compound **4a** and 23 mg (49%) of the more polar compound **7a** were obtained.

Reaction between Allenol 1b and IPy_2BF_4 in the Presence of $AuCl_3$. Preparation of Quinoline-2,3-dione 7b and Quinoline-2,4-dione 9. From 25 mg (0.12 mmol) of indolin-2-one-tethered allenol **1b**, and after chromatography of the residue using dichloromethane/ethyl acetate (20:1) as eluent, 5 mg (12%) of the less polar compound **9** and 16 mg (40%) of the more polar compound **7b** were obtained

Quinoline-2,3-dione 7b. Yellow solid; mp 183–185 ºC; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C) δ: 9.63 (br s, 1H), 7.37 (td, *J* = 7.8, 1.6 Hz, 1H), 7.30 (m, 1H), 7.20 (m, 1H), 7.02 (dd, *J* = 7.9, 1.0 Hz, 1H), 6.33 and 6.20 (d, *J* = 2.8 Hz, each 1H), 1.60 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C) δ: 191.7, 155.5, 133.6, 129.7, 129.6, 128.0, 126.9, 124.8, 117.0, 108.9, 62.9, 23.4; IR ($CHCl_3$, cm^{-1}): ν 3247, 1741, 1682; HRMS (ES): calcd for $C_{12}H_{11}INO_2$ [*M* + H]$^+$: 327.9834; found: 327.9823.

Quinoline-2,4-dione 9. Pale brown solid; mp 117–119 ºC; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C) δ: 8.48 (br s, 1H), 8.02 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.60 (td, *J* = 8.2, 1.5 Hz, 1H), 7.20 (td, *J* = 8.0, 1.0 Hz, 1H), 6.96 (d, *J* = 8.2 Hz, 1H), 6.53 and 6.23 (d, *J* = 2.8 Hz, each 1H), 1.70 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C) δ: 193.3, 171.7, 140.3, 136.6, 129.7, 128.6, 124.0, 118.5, 116.3, 103.0, 67.1, 22.9; IR ($CHCl_3$, cm^{-1}): ν 3245, 1705, 1670; HRMS (ES): calcd for $C_{12}H_{11}INO_2$ [*M* + H]$^+$: 327.9834; found: 327.9834.

General Procedure for the Reaction of 3-Allenyl 3-Hydroxyindolin-2-ones 1 with NCS in the Presence of Ag(I). A solution of the silver salt [Ag(phen)OTf] (6.2 mg, 0.014 mmol), 2,6-lutidine (0.007 mL, 0.056 mmol), the corresponding indolin-2-one-tethered allenol **1** (0.14 mmol), and *N*-chlorosuccinimide (24.4 mg, 0.18 mmol) in dichloromethane (2 mL) was heated in a sealed tube at 75^{o}C for 24 h. After cooling the reaction mixture to RT, saturated aqueous sodium hydrogen carbonate (5 mL) was added, before being partitioned between dichloromethane and water. The organic extract was washed with brine, dried ($MgSO_4$), concentrated under vacuum, and purified by flash column chromatography eluting with ethyl acetate/hexanes mixtures. Spectroscopic and analytical data for pure forms of compounds **10** and **11** follow.

Reaction between Allenol 1a and *N*-Chlorosuccinimide in the Presence of [Ag(phen)OTf]. Preparation of Quinoline-2,3-dione 10 and Quinoline-2,4-dione 11. From 30 mg (0.14 mmol) of indolin-2-one-tethered allenol **1a**, and after chromatography of the residue using hexanes/ethyl acetate (5:1) as eluent, 8 mg (22%) of the less polar compound **11** and 18 mg (51%) of the more polar compound **10** were obtained.

Quinoline-2,3-dione 10. Pale brown solid; mp 101–103 ºC; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C) δ: 7.44 (td, J = 8.1, 1.3 Hz, 1H), 7.36 (dd, J = 7.8, 1.3 Hz, 1H), 7.22 (m, 1H), 7.12 (d, J = 8.2 Hz, 1H), 5.53 and 5.25 (d, J = 2.5 Hz, each 1H), 3.49 (s, 3H), 1.75 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C) δ: 190.8, 156.2, 140.8, 137.5, 129.7, 127.6, 126.2, 124.6, 116.5, 115.8, 59.8, 30.2, 20.6; IR ($CHCl_3$, cm^{-1}): ν 1743, 1684; HRMS (ES): calcd for $C_{13}H_{13}ClNO_2$ $[M + H]^+$: 250.0635; found: 250.0629.

Quinoline-2,4-dione 11. Colorless solid; mp 97–99 ºC; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C) δ: 8.06 (dd, J = 8.0, 1.7 Hz, 1H), 7.68 (td, J = 8.3, 1.7 Hz, 1H), 7.22 (m, 2H), 5.63 and 5.60 (d, J = 2.6 Hz, each 1H), 3.53 (s, 3H), 1.69 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C) δ: 193.0, 170.1, 143.0, 138.7, 136.5, 128.6, 123.4, 119.8, 116.3, 114.9, 64.4, 30.1, 22.6; IR ($CHCl_3$, cm^{-1}): ν 1702, 1665, 1471, 1419 cm^{-1}; HRMS (ES): calcd for $C_{13}H_{13}ClNO_2$ $[M + H]^+$: 250.0635; found: 250.0628.

General Procedure for the Selective NBS-Promoted Indolin-2-one Ring Expansion Reaction. Controlled Preparation of Quinolinedione Derivatives 2a, 2c, and 2d. To a solution of the corresponding indolin-2-one-tethered allenol **1** (0.50 mmol) in dichloromethane (20 mL) was added *N*-bromosuccinimide (1.3 equiv). The reaction mixture was stirred at RT until the starting material disappeared as indicated by TLC. Saturated aqueous sodium hydrogen carbonate (5 mL) was added, before being partitioned between dichloromethane and water. The organic extract was washed with brine, dried ($MgSO_4$), concentrated under vacuum, and purified by flash column chromatography eluting with ethyl acetate/hexanes or dichloromethane/ethyl acetate mixtures. Spectroscopic and analytical data for pure forms of compounds **2** follow.

Quinoline-2,3-dione 2a. From 30 mg (0.14 mmol) of indolin-2-one-tethered allenol **1a**, and after chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent gave compound **2a** (36 mg, 86%) as a colorless solid; mp 93–95 ºC.

Quinoline-2,3-dione 2c. From 24 mg (0.10 mmol) of indolin-2-one-tethered allenol **1c**, and after chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent gave compound **2c** (26 mg, 80%) as a pale brown solid; mp 145–147 ºC.

Quinoline-2,3-dione 2d. From 25 mg (0.10 mmol) of indolin-2-one-tethered allenol **1d**, and after chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent gave compound **2d** (19 mg, 57%) as a colorless oil.

General Procedure for the Selective Palladium-Catalyzed Oxybromination of Indolin-2-one-Tethered Allenols 1. Controlled Preparation of Spirocyclic Bromodihydrofurans 5a, 5c, and 5d. Palladium(II) acetate (0.012 mmol), lithium bromide (0.66 mmol), potassium carbonate (0.16 mmol) and copper(II) acetate (0.28 mmol) were sequentially added to a stirred solution of the corresponding indolin-2-one-tethered allenol **1** (0.134 mmol) in acetonitrile (7 mL). The resulting suspension was stirred at room temperature under an oxygen atmosphere for 20 h at room temperature. The organic phase was diluted with brine (2 mL), extracted with ethyl acetate (3 x 5 mL), washed with brine (2 mL), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue eluting with hexanes/ethyl acetate mixtures gave analytically pure compounds **5**.

Spirocyclic Bromodihydrofuran 5a. From 45 mg (0.21 mmol) of indolin-2-one-tethered allenol **1a**, and after chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent gave compound **5a** (33 mg, 52%) as a colorless solid; mp 230–231 ºC.

Spirocyclic Bromodihydrofuran 5c. From 50 mg (0.20 mmol) of indolin-2-one-tethered allenol **1c**, and after chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent gave compound **5c** (33 mg, 50%) as a pale brown oil.

Spirocyclic Bromodihydrofuran 5d. From 54 mg (0.22 mmol) of indolin-2-one-tethered allenol **1d**, and after chromatography of the residue using hexanes/ethyl acetate (4:1) as eluent gave compound **5d** (35 mg, 48%) as a pale brown oil.

Reaction of Indolin-2-one-Tethered Allenol 1a in the Presence of Au(III). Preparation of Spirocyclic Dihydrofuran 15. A solution of the indolin-2-one-tethered allenol **1a** (90 mg, 0.42 mmol) and $AuCl_3$ (0.021 mmol) in dichloromethane (8.5 mL) was stirred at RT until the starting material disappeared as indicated by TLC (1 h). Saturated aqueous sodium hydrogen carbonate (4 mL) was added, before being partitioned between dichloromethane and water. The organic extract was washed with brine, dried ($MgSO_4$), concentrated under vacuum, and purified by flash column chromatography using hexanes/ethyl acetate (2:1) as eluent to give compound **15** (88 mg, 98%) as a colorless oil; ^{1}H-NMR (300 MHz, $CDCl_3$, 25 ^{o}C) δ: 7.32 (td, J = 7.7, 1.2 Hz, 1H), 7.20 (d, J = 6.3 Hz, 1H), 7.07 (t, J = 7.5 Hz, 1H), 6.82 (d, J = 7.7 Hz, 1H), 5.96 (q, J = 1.5 Hz, 1H), 5.01 and 4.90 (dt, J = 12.4, 1.9 Hz, each 1H) 3.20 (s, 3H), 1.43 (q, J = 1.9 Hz, 3H); ^{13}C-NMR (175 MHz, $CDCl_3$, 25 ^{o}C) δ: 175.6, 144.0, 135.8, 130.0, 128.3, 124.9, 124.4, 123.1, 108.2, 92.4,76.3, 26.3, 11.1; IR ($CHCl_3$, cm^{-1}): ν 1715; HRMS (ES): calcd for $C_{13}H_{13}NO_2$ $[M + H]^+$: 216.1025; found: 216.1031.

General Procedure for the Reaction of Spirocyclic Dihydrofurans 15 and 4a with NBS in the Presence of Au(III). A solution of the gold salt (0.005 mmol) and *N*-bromosuccinimide (0.26 equiv) in dichloromethane (2 mL) was stirred for five minutes. Then, a solution of the corresponding spirocyclic dihydrofuran (0.10 mmol) in dichloromethane (2 mL) was added. The reaction mixture was stirred at RT until the starting material disappeared as indicated by TLC. Saturated aqueous sodium hydrogen carbonate (1 mL) was added, before being partitioned between dichloromethane and water. The organic extract was washed with brine, dried ($MgSO_4$), concentrated under vacuum, and purified by flash column chromatography eluting with ethyl acetate/hexanes mixtures.

Spirocyclic 5-Bromooxindole 3a. From 20 mg (0.093 mmol) of spirocyclic dihydrofuran **15**, and after chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent gave

compound **3a** (26 mg, 95%) as a colorless oil.

Spirocyclic 5-Bromooxindole 18. From 18 mg (0.052 mmol) of spirocyclic iododihydrofuran **4a**, and after chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent gave compound **18** (14 mg, 66%) as a yellow oil; ^{1}H-NMR (700 MHz, $CDCl_3$, 25 ^{o}C) δ: 7.47 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.30 (d, *J* = 2.1 Hz, 1H), 6.72 (d, *J* = 2.1, 1H), 4.98 and 4.87 (m, each 1H), 3.18 (s, 3H), 1.47 (t, *J* = 2.1 Hz, 3H); ^{13}C-NMR (175 MHz, $CDCl_3$, 25 ^{o}C) δ: 173.7, 142.8, 138.7, 133.3, 129.3, 127.8, 124.6, 115.9, 109.9, 89.2, 82.7, 26.4, 13.0; IR ($CHCl_3$, cm^{-1}): ν 1714; HRMS (ES): calcd for $C_{13}H_{12}BrINO_2$[*M* + H]$^+$: 419.9096; found: 419.9075.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Copies of the ^{1}H NMR and ^{13}C NMR spectra for all new compounds. See DOI: 10.1039/b000000x/

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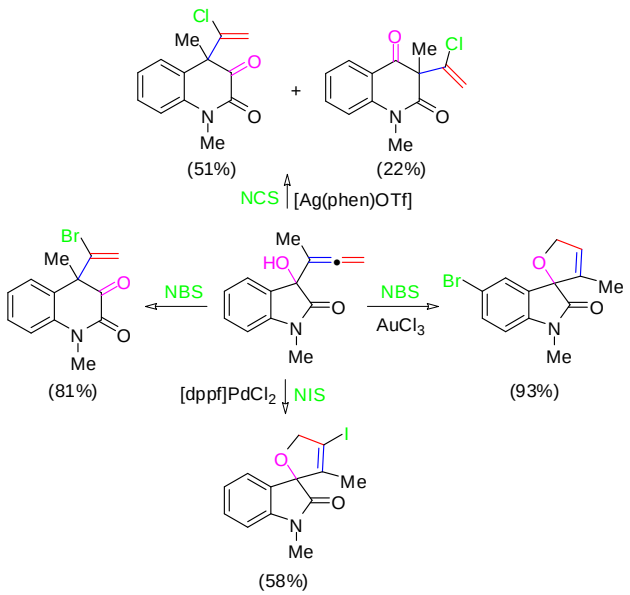
Graphical Abstract



The reactions of 3-allenyl 3-hydroxyoxindoles with a variety of halogenated reagents in the presence of catalytic amounts of precious metal salts were explored. Both, rearrangement and oxycyclization reactions to give 4-(1-halovinyl)-quinolinediones or spirocyclic halooxindoles, respectively, are competitive pathways.