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Difunctionalization of Alkenes Using 1-Chloro-1,2-benziodoxol-3-(1*H*)-one

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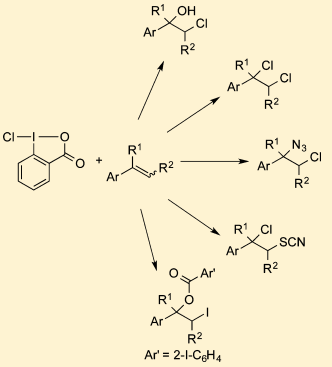
Supporting Information

ABSTRACT: Difunctionalization of alkenes with 1-chloro-1,2-benziodoxol-3-(1*H*)-one (**1**) was investigated. Various additional nucleophiles were tested, and oxychlorination, dichlorination, azidochlorination, chlorothiocyanation, and iodoesterfication were demonstrated. The oxychlorination product was obtained efficiently when the reaction was operated in water. Dichlorination occurred in the presence of a Lewis basic promoter, such as 4-phenylpyridine *N*-oxide, as an additive. The reaction with *in situ*-generated azido anion afforded azidochlorinated compounds with a chlorine atom at the terminal position, while the reaction with trimethylsilyl isothiocyanate produced chlorothiocyanation adducts with a chlorine atom at the benzylic position. On the other hand, when **1** was treated with tetra-*n*-butylammonium iodide prior to the addition of alkenes, only iodoesterification occurred selectively. These mild reactions enable convenient site-selective difunctionalizations of substrates having two alkene moieties. NMR experiments suggested that the electrophilic reactive species in each reaction varied depending on the nature of the added nucleophile.



INTRODUCTION

Difunctionalization of alkenes is a powerful tool for the synthesis of complex molecules, because two functional groups can be introduced into an organic framework at once.[1] Among various functional groups, chlorine is often found in natural products and bioactive compounds, and organochlorine compounds have also been utilized as useful building blocks. Although many methodologies are available to prepare organochlorine compounds,[2] difunctionalization-type chlorination of alkenes is one of the most attractive.[3]

We have previously reported several trifluoromethylation reactions of C−C multiple bonds with Togni reagent in the presence of copper catalyst,[4] and in the preparation of the Togni reagent, 1-chloro-1,2-benziodoxol-3-(1*H*)-one (**1**)[5,6] is synthesized as a precursor for ligand exchange reaction with a trifluoromethyl anion (Scheme 1a).[7] During the course of our investigation, we became interested in the reactivity of **1**.

Among chlorine-containing hypervalent iodine reagents, iodobenzene dichloride is a representative reagent for chlorofunctionalization of alkenes. For example, Nicolaou et al. achieved asymmetric dichlorination of allylic alcohols using a dimeric cinchona alkaloid derivative as a catalyst,[8] and Du and Zhao et al. recently reported oxychlorination of alkenes using iodobenzene dichloride in DMF.[9] However, the utility of such reagents in difunctionalization of alkenes has not been thoroughly examined. Furthermore, the reactivity of **1** toward organo-functional groups has not been studied, except in a few cases. For example, **1** was used as a terminal oxidant in alcohol oxidation with 2,2,6,6-tetramethylpyrrolidine *N*-oxide (TEMPO).[10] As for the use of **1** as an electrophilic chlorination reagent, there are only two reports describing chlorination of 1,2,4,5-tetramethylbenzene (durene) in acetic acid[11a] and α-chlorination of β-dicarbonyl compounds (Scheme 1b).[11b] Since **1** would undergo rapid ligand exchange reaction with added nucleophile X, we expected that various types of reactive species could be formed (Scheme 1c).[12] For example, substitution by an electronically neutral Lewis base would give a more Lewis-acidic hypervalent iodine(III), and ligand exchange reaction followed by reductive elimination would give Cl−X species. Thus, the nature of the added nucleophile may influence the reaction pathway, opening up the possibility of obtaining unique difunctionalization products. To investigate differences in reactivity and synthetic utility compared to other chlorinating reagents, we examined the use of **1** for difunctionalization of alkenes with various nucleophiles. In this report, we present various reactions of styrene derivatives with 1-chloro-1,2-benziodoxol-3-(1*H*)-one **1**, including oxychlorination,[13] dichlorination,[14] azidochlorination,[15] chlorothiocyanation,[16] as well as iodoesterification[17] (Scheme 1d).

RESULTS AND DISCUSSION

Development of Difunctionalization of Alkenes with 1. *1. Reaction with Water.* Initially, oxychlorination of alkenes was selected as a test reaction for investigating the reactivity of the chlorination reagent **1**, because the corresponding product, chlorohydrin, represents an important class of substructures in organic synthesis.[13] With reference to previous reports on oxychlorination,[18] we carried out the reaction in a mixture of acetone/H_2O as a solvent. Although the reaction proceeded

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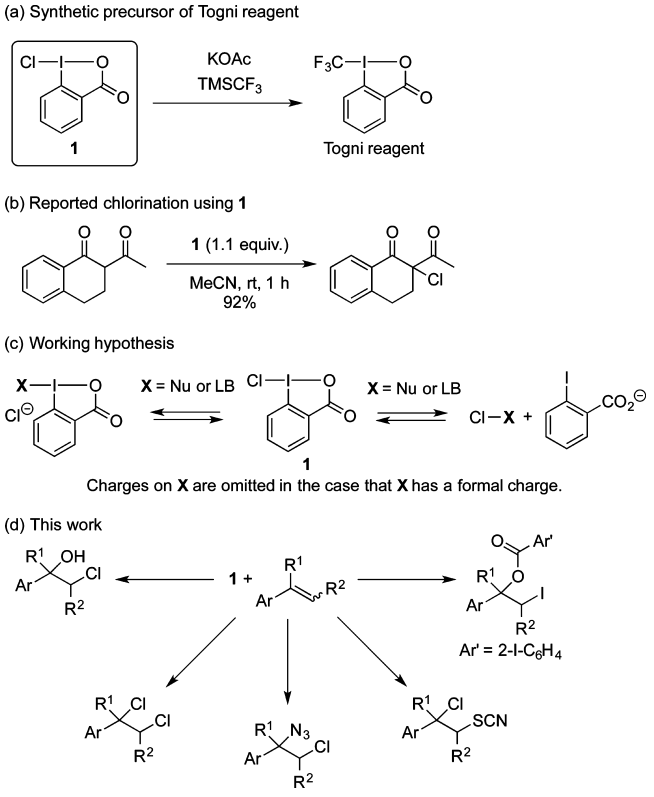
Scheme 1. Use of 1-Chloro-1,2-benziodoxol-3-(1*H*)-one (1)

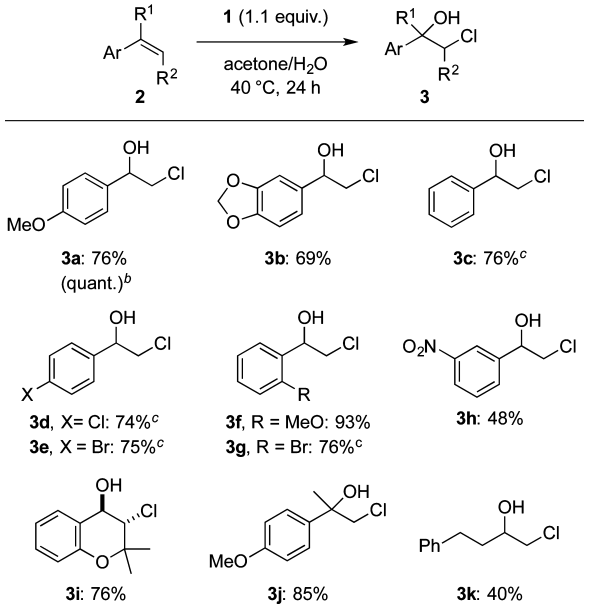


slowly at room temperature, chlorohydrins were cleanly formed at 40 °C (Table 1). The reactions with electron-rich **2a** and **2b** provided the corresponding chlorohydrins in 76% and 69% isolated yields, respectively. This reaction could also be applied to styrene derivatives having no electron-donating groups, and good to high yields were generally obtained (**3c**−**3e**). In addition, *ortho*-substituted styrenes were applicable to provide corresponding products **3f** and **3g** in high yields, while the substrate having an strongly electron-withdrawing group, such as a nitro group, was transformed in only 48% yield (**3h**). The reaction of geminally and vicinally disubstituted alkenes proceeded smoothly to give **3i** and **3j** in 76% and 85% yields, respectively. Reactions of aliphatic alkene **2k** afforded **3k** in 40% yield, though dichlorination also proceeded as an undesired reaction.

2. Reaction with Pyridine N-Oxide. We next attempted to use pyridine *N*-oxide as an oxygen-based nucleophile, expecting that the corresponding *N*-oxide adduct would undergo elimination of pyridine to give *α*-chloroketones. However, no *N*-oxide adduct was formed. Instead, the dichlorination product was formed cleanly in nonprotic solvent (Table 2).[19] Addition of 4-phenylpyridine *N*-oxide gave better results for all the substrates examined. It is considered that the *N*-oxide acted as a Lewis basic promoter for **1**, and not as an actual nucleophile; the second chloride ion would come from substitution reaction of a chloride ion within **1** by pyridine *N*-oxide. Thus, we also examined the reaction with tetrabutylammonium chloride (TBAC) in place of the combination of pyridine *N*-oxide and **1**, but this reaction afforded a lower yield (~50% yield).

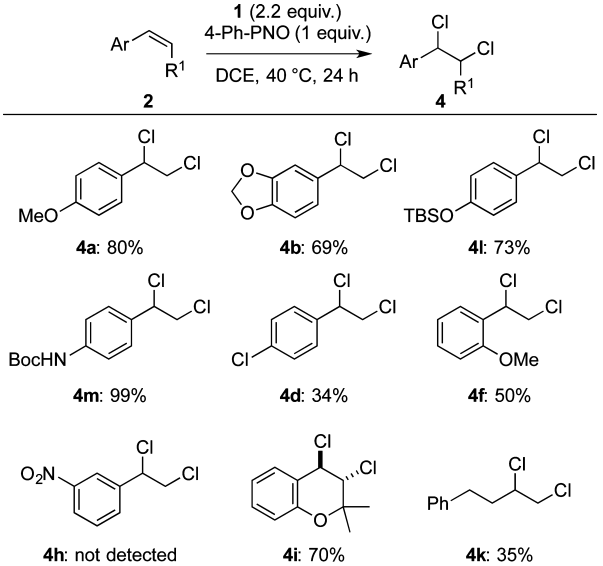
All dichlorination products were isolated by a recycle gel permeation chromatography (GPC) system with polystyrene/divinylbenzene porous polymer, because of the instability of some products in the presence of silica gel. In dichloroethane (DCE), the reaction of styrene derivatives bearing electron-donating groups proceeded smoothly at 40 °C, affording the corresponding products (**4a**,**b**,**l**,**m**) in good yields. Although 4-chlorostyrene **2d** reacted slowly, the desired product **4d** was obtained in 34% yield, together with the 2-chlorostyrene derivative (20% yield) as a byproduct. A more electron-deficient one did not provide the corresponding dichlorination product. For example, no reaction occurred in the reaction of

Table 1. Oxychlorination in Acetone/Water[a]



[a]The reactions were carried out with **1** (1.1 equiv) at 40 °C in acetone/water on a 0.2 mmol scale, unless otherwise mentioned. [b]Determined by ^{1}H NMR analysis by using 1,1,2,2-tetrachloroethane as an internal standard. [c]Run with 1.5 equiv of **1**.

Table 2. Dichlorination with 4-Ph-pyridine *N*-oxide (4-Ph-PNO)



[a]The reactions were carried out with **1** (2.2 equiv) and 4-phenylpyridine-*N*-oxide (1 equiv) at 40 °C in 1,2-dichloroethane on a 0.2 mmol scale.

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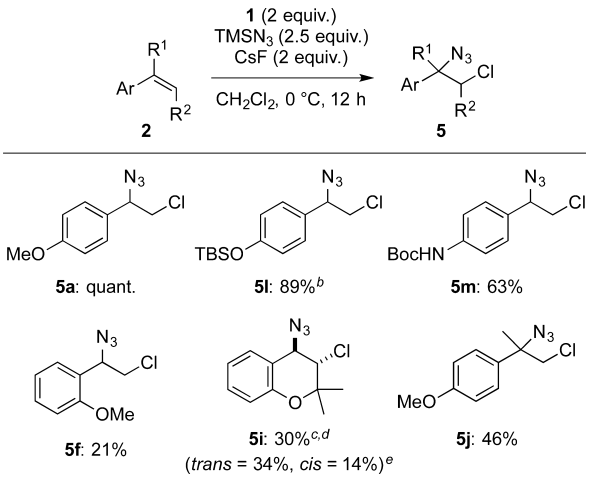
2h. An *ortho*-substituted substrate **2f** provided dichlorination product **4f** (50%) and the corresponding 2-chlorostyrene derivative (34%). This reaction was also applicable to benzopyran **2i**, giving the corresponding dichloride **4i** in 70% yield. Although some unidentified byproducts were detected by NMR analysis of the crude mixture, aliphatic product **4k** was isolated in 35% yield.

3. Reaction with Trimethylsilyl Azide ($TMSN_3$). Having confirmed that **1** can act as a mild electrophilic chlorinating reagent, we turned our attention to the introduction of a nitrogen functional group. Thus, trimethylsilyl azide ($TMSN_3$) was added as an external nucleophile to the reaction mixture of **1** and the substrates in nonprotic solvent. Although the reaction without an additive was sluggish, the addition of fluoride ion to generate azide anion was effective to accelerate the desired azidochlorination reaction. Screening of the reaction conditions revealed that CsF was the fluoride ion source of choice.[19] Furthermore, the reaction temperature was crucial to control the regioselectivity; a significant amount of the regioisomer was formed as a byproduct when the reaction was run at 40 °C.

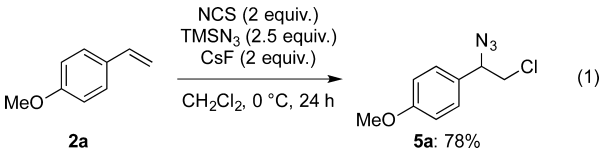
Similarly to the other reactions, electron-donating groups on the aryl ring facilitated the reaction, and the products (**5a,l,m**) were obtained in good to high yields (Table 3). In the case of

Table 3. Azidochlorination Using 1 with $TMSN_3$[a]



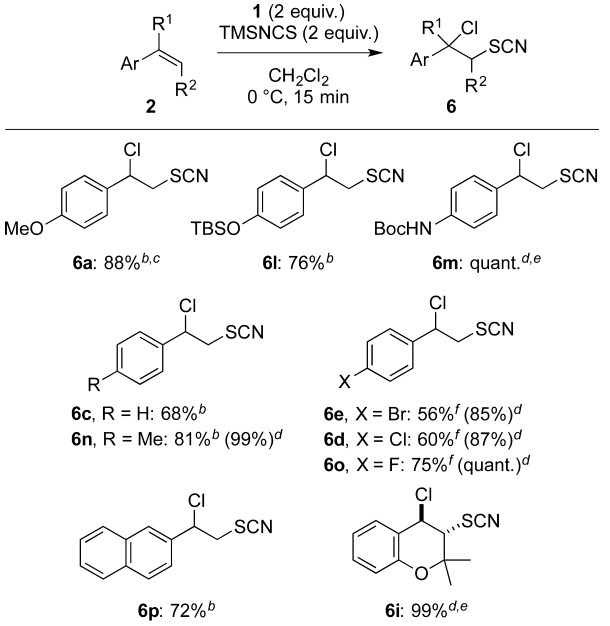
[a]The reactions were carried out with **1** (2 equiv), $TMSN_3$ (2.5 equiv), CsF (2 equiv) at 0 °C in CH_2Cl_2 on a 0.2 mmol scale, unless otherwise mentioned. [b]Run for 24 h. [c]Run at −15 °C. [d]Isolated yield of *trans*-isomer. [e]Determined by ^1H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard.

2i, signals of the corresponding regioisomer were detected in the ^1H NMR spectrum of the crude mixture when the reaction was performed at 0 °C. However, when the reaction was performed at −15 °C, no regioisomer was detected, and **5i** was obtained in 48% NMR yield (*trans*/*cis* = 34%/14%). An *ortho*-substituent on the aryl ring retarded the formation of desired product **5f**, and dichlorination product **4f**, 2-chlorostyrene derivative, and 2-chloro-2′-methoxyacetophenone were observed as byproducts. Again, the disubstituted substrate **2j** could be used, and the product **5j** was isolated in 46% yield. In these reactions, incorporation of a fluorine atom was not observed. When the reaction of 3-nitrostyrene **2h** was carried out under the standard conditions, a trace amount of the azidochlorination product was detected in the ^1H NMR spectrum of the crude mixture. Incidentally, the use of *N*-chlorosuccinimide (NCS), a commonly used chlorinating reagent, for azidochlorination of alkenes is quite rare, to our knowledge.[15c] To compare the utility of this reagent, the reaction with NCS instead of **1** was examined under the similar reaction conditions (eq 1). As a result, azidochlorination proceeded to give **5a** in 78% yield after 24 h, suggesting that the reaction with **1** is faster than that with NCS.



4. Reaction with (Trimethylsilyl)isothiocyanate (TMSNCS). Following the azidochlorination with $TMSN_3$, chlorothiocyanation of alkenes, which has rarely been reported,[16] was next examined with TMSNCS (Table 4). Unlike the azidochlorination, the reaction did not require the addition of a fluoride ion source. The ratio between **1** and TMSNCS was important for this reaction, because when the reaction was conducted with an excess of TMSNCS, dithiocyanation occurred as a side reaction. The structure of the resulting product was unambiguously determined from the HMBC and HSQC spectra.[19] It is noteworthy that the chlorine atom was introduced at the benzylic position, which is distinct from other reactions (*vide supra*). The reaction was completed within only 15 min, and good to high yields were obtained with not only electron-rich but also electron-poor substrates. Since most of the products were not stable on silica gel, purification was performed using a recycle GPC system. In the case of substrates having an electron-withdrawing group, the corresponding products could

Table 4. Chlorothiocyanation Using 1 with TMSNCS[a]



[a]The reactions were carried out with **1** (2 equiv) and TMSNCS (2 equiv) in CH_2Cl_2 on a 0.2 mmol scale. [b]Isolated using a GPC system. [c]Run for 1 h. [d]Determined by NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard. [e]These compounds could not be isolated due to their instability. [f]Isolated by chromatography on silica gel.

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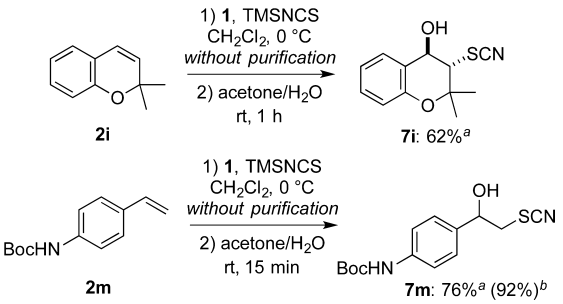
tolerate silica gel chromatography (**6d** and **6o**). Since partial decomposition of **6i** and **6m** occurred even during purification by GPC, the thiocyanation products were isolated after transformation of **6**. Thus, treatment of the crude reaction products with acetone/H_2O at room temperature gave more stable oxythiocyanation compounds **7i** and **7m** in 62% and 76% isolated yield, respectively (Scheme 2). Additionally, the high

Scheme 2. Transformation of Chlorothiocyanation Products

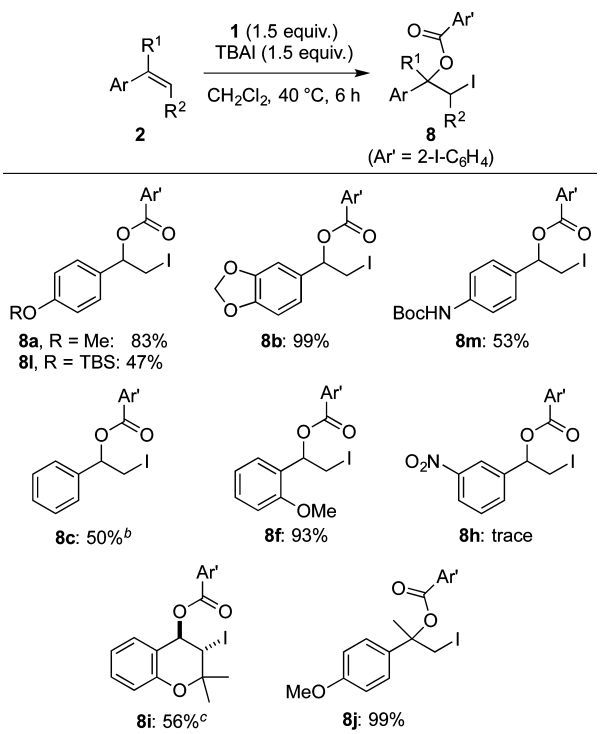


[a]Isolated yield. [b]Determined by NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard.

reactivity of this reaction enabled difunctionalization of cyclohexene.[16b] It should be noted that a complex mixture was formed when NCS was used instead of **1**, indicating the mild reactivity of the present reagent combination.

5. Reaction with Tetra-n-butylammonium Iodide (TBAI). During further screening of the reaction conditions, we found that the combination of **1** and TBAI selectively afforded the corresponding iodoesterification products **8** in good to high yields (Table 5). As in the case of the chloro-difunctionalization

Table 5. Iodoesterification Using 1 with TBAI[a]

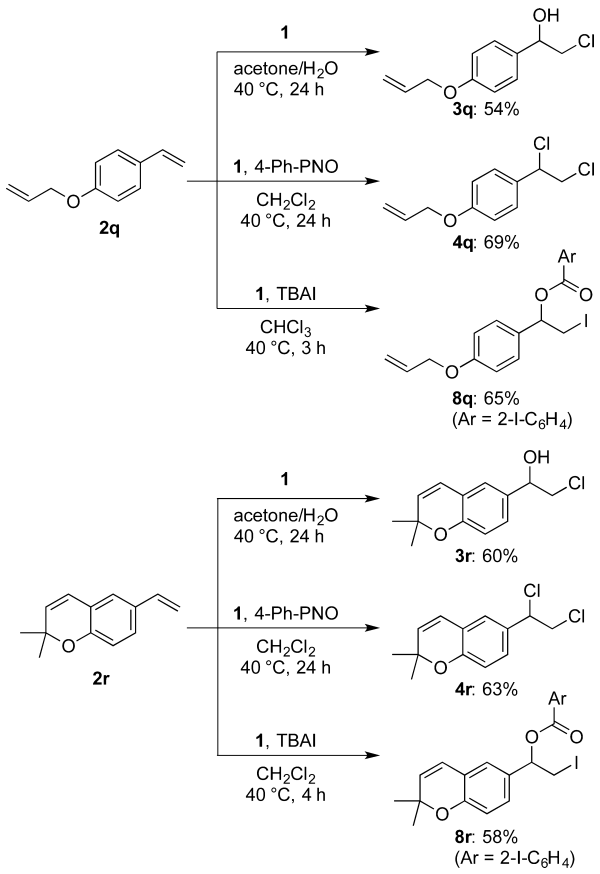


[a]The reactions were carried out with **1** (1.5 equiv) and TBAI (1.5 equiv) in CH_2Cl_2 at 40 °C on a 0.2 mmol scale, unless otherwise mentioned. [b]Run with 3 equiv of TBAI. [c]Run at 60 °C.

reactions, some functional groups were tolerant of these reaction conditions. The regioselectivity was the same as that observed in preceding oxyiodination reactions, including the reaction using the combination of iodobenzene dichloride and iodine in MeOH, which was reported by Yusubov and co-workers.[20] The reactions of electron-rich substrates proceeded smoothly, and the corresponding products were obtained in good to high yields, irrespective of the position of substituents. In contrast, a trace amount of product **8h** was observed in the reaction of **2h** having a nitro group. In the case of 4-phenyl-1-butene **2k**, an inseparable mixture of some unidentified products was obtained.

6. Site-Selective Difunctionalization. As described above, **1** seems to show mild reactivity compared with other halogenation reagents. Taking advantage of this feature, we expected that site-selective functionalization of substrates having multiple olefins would be possible. Thus, we investigated the difunctionalization reactions of substrates bearing two olefin moieties (**2q** and **2r**) (Scheme 3). To our

Scheme 3. Site-Selective Difunctionalization



delight, site-selective reactions occurred: In the case of **2q**, only the styrene moiety reacted to give the corresponding products **3q**, **4q**, and **8q**, due to the higher reactivity of the conjugated alkene compared with the allylic ether moiety. In addition, **3r**, **4r**, and **8r** were selectively obtained in the reaction of **2r**. These results suggest that the reaction of **1** would be sensitive to steric hindrance at the reaction site.

Mechanistic Discussion. In general, difunctionalization of alkenes using a hypervalent iodine reagent is thought to proceed through the coordination of alkenes to the hypervalent iodine atom to generate an iodonium cation and/or the

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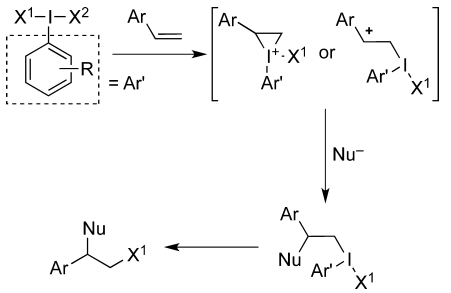
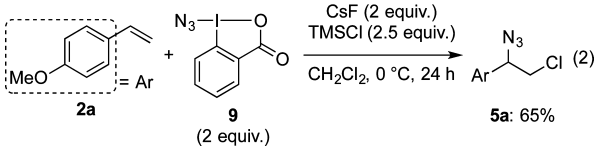
corresponding carbocation.[1a,12,21] In the light of the proposed reaction mechanism of dioxy-functionalization of alkenes,[21] the oxychlorination and the dichlorination could be explained by a similar mechanism, as shown in Scheme 4. Thus, the first nucleophile in each reaction attacks at the benzylic position, and substitution reaction by a chloride ion occurs at the terminal position.

Scheme 4. Typical Mechanism of Alkene Difunctionalization Using a Hypervalent Iodine Reagent



Although a similar reaction mechanism might be applicable to other difunctionalization reactions, the following results let us to probe the actual reactive species in aziochlorination and chlorothiocyanation: (1) The combination of TMSCl, CsF, and azido-type hypervalent iodine reagent **9**[22] provided the same product **5**, and not the regioisomer (eq 2 and Table 3),



suggesting that the same chemical species is operative in both reactions. (2) The regioselectivity of azidochlorination and that of chlorothiocyanation are complementary to each other.

First, we measured the ^{1}H NMR spectrum of a 1:1:1 mixture of **1**, $TMSN_3$, and CsF (Figure 1). At the initial stage, in addition to **1** and **9**, trimethylsilyl 2-iodobenzoate was detected (Figure 1a). The amount of **1** continued to decrease over the initial 2.5 h (Figure 1b), while that of **9** gradually increased. The reaction of **9** with TMSCl and CsF after 30 min gave a mixture similar to that shown in Figure 1a, in which the formation of a larger amount of trimethylsilyl 2-iodobenzoate was observed (Figure 2a). After 2.5 h, both **1** and **9** were clearly observed, while trimethylsilyl 2-iodobenzoate was no longer detected, as was seen in Figure 1b (Figure 2b). The formation of trimethylsilyl 2-iodobenzoate at the initial stage suggested the generation of chlorine azide (ClN_3) in the reaction mixture, and the disappearance of trimethylsilyl 2-iodobenzoate after 2.5 h might be associated with reoxidation of 2-iodobenzoate by ClN_3 to regenerate hypervalent iodine reagents. When styrene derivative **2a** was added to the reaction mixture of **1**, $TMSN_3$, and CsF after 2.5 h (Figure 1b), no reaction occurred, indicating that neither **1** nor **9** could react with olefins. However, upon further addition of TMSCl to this reaction mixture, which might allow regeneration of ClN_3, the azidochlorination proceeded at 0 °C together with formation of the regioisomer and dichlorination products. Based on these results, we speculate that ClN_3 is the actual reactive species in this azidochlorination, although intermediate **10** generated *in*

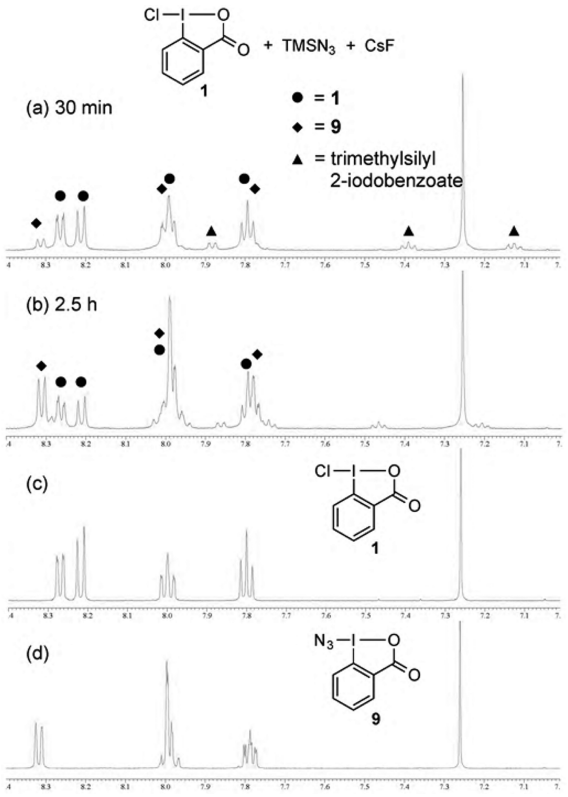


Figure 1. ^{1}H NMR study of azidochlorination.

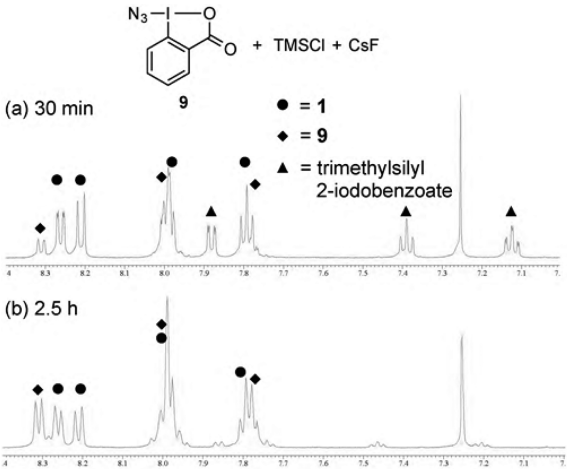


Figure 2. ^{1}H NMR spectra of the mixture of **9**, TMSCl, and CsF.

situ cannot be ruled out at present (Scheme 5).[15b] In the reaction with **9** (eq 2), the yield was decreased to 65% compared with the reaction with **1** (Table 3), and some unidentified byproducts were detected by ^{1}H NMR analysis of the crude mixture. We think that this might be due to the higher concentration of highly reactive ClN_3 at the initial stage of the reaction starting from **9**.

To examine chlorothiocyanation, we also conducted NMR experiments using a mixture of **1** and TMSNCS in $CDCl_3$. In this case, most of compound **1** disappeared quickly, and peaks of trimethylsilyl 2-iodobenzoate were observed clearly (Figure 3a). Thus, we considered that thiocyanogen chloride (Cl–SCN) would be an active species in this reaction (Scheme 6).[23] The involvement of Cl–SCN can explain the observed

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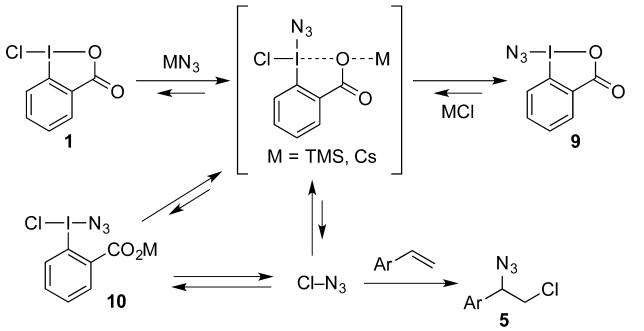
Scheme 5. Proposed Mechanism of Azidochlorination



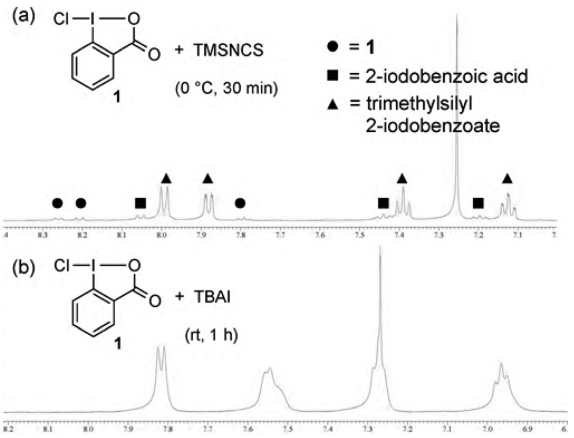
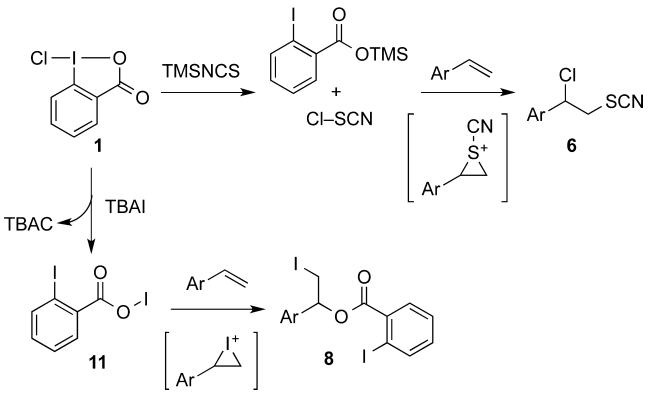


Figure 3. ^{1}H NMR studies of chlorothiocyanation and iodoesterification.

Scheme 6. Proposed Mechanism of Chlorothiocyanation and Iodoesterfication



regioselectivity (Table 4). The σ^* orbital of the S−Cl bond would interact with alkene to give a three-membered thionium ion, which is opened by attack of the remaining chloride ion (Scheme 6). It should be noted that Cl−SCN can be formed readily from easy-to-handle reagent **1**, while the previous procedures required gaseous chlorine (Cl_2).[16,23]

The reaction of **1** with TBAI was also monitored by ^{1}H NMR analysis. Although the signals were broad, the pattern was quite similar to that of 2-iodobenzoic acid, except that the signals were shifted to higher magnetic field. According to the literature, these peaks are not due to the tetra-*n*-butylammonium salt of 2-iodobenzoate.[24] Thus, it seems likely that hypoiodous compound **11** is generated.[25] The structure and regioselectivity of the product can be understood in terms of the inherent reactivity of putative intermediate **11** (Scheme 6).

CONCLUSION

The reactivity of **1** toward alkenes was investigated. Oxychlorination, dichlorination, azidochlorination, chlorothiocyanation, and iodoesterification were achieved with appropriate nucleophiles and reaction conditions. In addition, chemoselective difunctionalizations were successfully achieved, reflecting the mild reactivity of these reactions. The nature of the reactive intermediates in each reaction was investigated by means of NMR experiments, which indicated that hypervalent iodine reagent **1** can generate various active species in the presence of appropriate additives. Further applications of **1** toward other functional groups are ongoing in our laboratory.

EXPERIMENTAL SECTION

General Experimental. Chemical shifts are reported downfield from TMS (= 0) or $CDCl_3$ for ^{1}H NMR. For ^{13}C NMR, chemical shifts are reported in the scale relative to $CDCl_3$. Infrared spectra were measured with KBr plate, and only diagnostic absorptions of infrared spectra are listed below. Column chromatography was performed with silica gel N-60 (40−100 mm). As described in the Results and Discussion section, purification was carried out using a recycling preparative HPLC system, if necessary. TLC analysis was performed on Silica gel 60 F_{254}-coated glass plates. Visualization was accomplished by means of ultraviolet (UV) irradiation at 254 nm or by spraying 12-molybdo(VI)phosphoric acid ethanol solution as the developing agent. Dehydrated dichloromethane (CH_2Cl_2), dichloroethane (DCE), acetone, $TMSN_3$, TMSNCS, 4-phenylpyridine *N*-oxide (4-Ph-PNO), CsF, and TMSCl were obtained from commercial sources, and used as received. 1-Chloro-1,2-benziodoxol-3-(1*H*)-one **1** was prepared according to the literature.[7]

Typical Procedure for Oxychlorination. To a solution of **1** (62 mg, 0.22 mmol) in acetone/H_2O (2 mL/2 mL) was added 4-methoxystyrene **2a** (26 μL, 0.2 mmol) at 40 °C. The mixture was stirred for 24 h at the same temperature, then quenched with sat. $NaHCO_3$, and diluted with ethyl acetate and H_2O. The organic phase was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (*n*-hexane/ethyl acetate = 10/1) to provide **3a** (28.2 mg, 76%).

*2-Chloro-1-(4-methoxyphenyl)ethan-1-ol (**3a**).* Colorless oil; 28.2 mg, 76%; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.31 (d, J = 8.8 Hz, 2H), 6.90 (d, J = 8.8 Hz, 2H), 4.85 (dd, J = 3.6, 8.7 Hz, 1H), 3.81 (s, 3H), 3.70 (dd, J = 3.6, 11.1 Hz, 1H), 3.63 (dd, J = 8.7, 11.1 Hz, 1H), 2.66 ppm (brs, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.7, 132.1, 127.3, 114.0, 73.7, 55.3, 50.9 ppm; IR ($CHCl_3$): 3599, 3009, 1613, 1513, 1249 cm^{-1}; HRMS (ESI$^+$-TOF): Calcd for $[C_9H_{11}ClO_2 + H]^+$: m/z = 187.0520, Found: 187.0518.

*1-(Benzo[d][1,3]dioxol-5-yl)-2-chloroethan-1-ol (**3b**).* Colorless solid; 27.6 mg, 69%; Mp 94−95 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.88 (d, J = 1.3 Hz, 1H), 6.83 (dd, J = 1.3, 7.9 Hz, 1H), 6.79 (d, J = 7.9 Hz, 1H), 5.96 (s, 2H) 4.80 (dd, J = 3.4, 8.6 Hz, 1H), 3.68 (dd, J = 3.4, 11.3 Hz, 1H), 3.60 (dd, J = 8.6, 11.3 Hz, 1H), 2.66 ppm (brs, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 147.9, 147.6, 133.9, 119.7, 108.3, 106.5, 101.2, 73.9, 50.8 ppm; IR ($CHCl_3$): 3595, 3032, 1489, 1446, 1246 cm^{-1}; HRMS (ESI$^+$-TOF): Calcd for $[C_9H_9ClO_3 + Na]^+$: m/z = 223.0132, Found: 223.0142.

*2-Chloro-1-phenylethan-1-ol (**3c**).* Colorless oil; 23.6 mg, 76%; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.40−7.32 (m 5H), 4.91−4.90 (m, 1H), 3.75 (dd, J = 3.4, 11.2 Hz, 1H), 3.65 (dd, J = 9.1, 11.2 Hz, 1H), 2.69 ppm (d, J = 2.3 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 139.9, 128.7, 128.4, 126.0, 74.1, 50.9 ppm; IR ($CHCl_3$): 3595, 3035, 3009, 1454, 1238, 1192 cm^{-1}; HRMS (ESI$^+$-TOF): Calcd for $[C_8H_9ClO + H]^+$: m/z = 157.0415, Found: 157.0416.

*2-Chloro-1-(4-chlorophenyl)ethan-1-ol (**3d**).* Colorless solid; 28.3 mg, 74%; Mp 33−34 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.37−7.32

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(m, 4H), 4.89 (ddd, J = 3.4, 3.4, 8.6 Hz, 1H), 3.72 (dd, J = 3.4, 11.0 Hz, 1H), 3.61 (dd, J = 8.6, 11.0 Hz, 1H), 2.65 ppm (d, J = 3.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 138.3, 134.2, 128.8, 127.4, 73.3, 50.7 ppm; IR ($CHCl_3$): 3595, 3007, 1597, 1492 cm^{-1}; HRMS (ESI$^+$-TOF): Calcd for $[C_8H_8Cl_2O + Na]^+$: m/z = 212.9844, Found: 212.9842.

*1-(4-Bromophenyl)-2-chloroethan-1-ol (**3e**).* Colorless oil; 35.1 mg, 75%; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.51 (d, J = 8.2 Hz, 2H), 7.27 (d, J = 8.2 Hz, 2H), 4.87 (ddd, J = 3.4, 3.4, 8.6 Hz, 1H), 3.72 (dd, J = 3.4, 11.3 Hz, 1H), 3.60 (dd, J = 8.5, 11.3 Hz, 1H), 2.69 ppm (d, J = 3.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 138.8, 131.8, 127.7, 122.4, 73.4, 50.6 ppm; IR ($CHCl_3$): 3595, 1593, 1489, 1072 cm^{-1}; HRMS (ESI$^+$-TOF): Calcd for $[C_8H_8BrClO + Na]^+$: m/z = 256.9339, Found: 256.9350.

*2-Chloro-1-(2-methoxyphenyl)ethan-1-ol (**3f**).* Colorless oil; 34.8 mg, 93%; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.44 (d, J = 7.5 Hz, 1H), 7.32−7.28 (m, 1H), 7.00 (dd, J = 7.5, 7.5 Hz, 1H), 6.89 (d, J = 8.6 Hz, 1H), 5.15−5.12 (m, 1H), 3.87−3.84 (m, 4H), 3.64 (dd, J = 8.6, 10.9 Hz, 1H), 2.92 ppm (d, J = 5.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 156.2, 129.2, 127.8, 127.2, 120.8, 110.4, 70.4, 55.3, 49.5 ppm; IR ($CHCl_3$): 3586, 2962, 1603, 1492, 1287 cm^{-1}; HRMS (ESI$^+$-TOF): Calcd for $[C_9H_{11}ClO_2 - HCl + H]^+$: m/z = 151.0754, Found: 151.0754.

*2-Chloro-1-(2-bromophenyl)ethan-1-ol (**3g**).* Colorless oil; 36.0 mg, 76%; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.63 (dd, J = 1.7, 7.7 Hz, 1H), 7.55 (dd, J = 1.2, 8.0 Hz, 1H), 7.39−7.36 (m, 1H), 7.21−7.18 (m, 1H), 5.27 (ddd, J = 2.9, 3.4, 8.9 Hz, 1H), 3.92 (dd, J = 2.9, 11.5 Hz, 1H), 3.54 (dd, J = 8.9, 11.5 Hz, 1H), 2.74 ppm (d, J = 3.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 138.8, 132.8, 129.8, 127.8, 127.7, 121.9, 72.9, 49.5 ppm; IR ($CHCl_3$): 3587, 3065, 1570, 1497, 1029 cm^{-1}; HRMS (ESI$^+$-TOF): Calcd for $[C_8H_8BrClO - HCl + H]^+$: m/z = 198.9753, Found: 198.9753.

*2-Chloro-1-(3-nitrophenyl)ethan-1-ol (**3h**).* Colorless oil; 19.5 mg, 48%; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.30 (s, 1H), 8.20 (d, J = 8.0 Hz, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.58 (dd, J = 8.0, 8.0 Hz, 1H), 5.04 (ddd, J = 3.4, 4.0, 8.3 Hz, 1H), 3.81 (dd, J = 3.4, 11.5 Hz, 1H), 3.67 (dd, J = 8.3, 11.5 Hz, 1H), 2.80 ppm (d, J = 4.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 148.4, 142.0, 132.2, 129.6, 123.3, 121.2, 72.9, 50.4 ppm; IR ($CHCl_3$): 3034, 1703, 1533, 1265 cm^{-1}; HRMS (ESI$^+$-TOF): Calcd for $[C_8H_8ClNO_3 + H]^+$: m/z = 202.0265, Found: 202.0266.

*3-Chloro-2,2-dimethylchroman-4-ol (**3i**).* Colorless solid; 32.2 mg, 76%; Mp 77−78 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.48 (d, J = 7.9 Hz, 1H), 7.23−7.20 (m, 1H), 7.00−6.97 (m, 1H), 6.81 (dd, J = 1.1, 8.5 Hz, 1H), 4.79 (d, J = 9.1 Hz, 1H), 3.99 (d, J = 9.1 Hz, 1H), 2.55 (brs 1H), 1.57 (s, 3H), 1.34 ppm (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 151.8, 129.7, 127.5, 122.4, 121.1, 116.9, 78.9, 70.1, 68.4, 27.7, 19.1 ppm; IR ($CHCl_3$): 3588, 3009, 1586, 1485, 1196 cm^{-1}; HRMS (ESI$^+$-TOF): Calcd for $[C_{11}H_{13}ClO_2 + Na]^+$: m/z = 235.0496, Found: 235.0495.

*1-Chloro-2-(4-methoxyphenyl)propan-2-ol (**3j**).* Colorless oil; 34.3 mg, 85%; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.39 (d, J = 9.1 Hz, 2H), 6.90 (d, J = 9.1 Hz, 2H), 3.81−3.79 (m, 4H), 3.72 (d, J = 10.5 Hz, 1H), 2.56 (brs, 1H), 1.63 ppm (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.9, 136.3, 126.2, 113.7, 73.5, 55.5, 55.2, 27.2 ppm; IR ($CHCl_3$): 3568, 3035, 3005, 1612, 1512, 1246, 1180 cm^{-1}; HRMS (ESI$^+$-TOF): Calcd for $[C_{10}H_{13}ClO_2 + Na]^+$: m/z = 223.0496, Found: 223.0488.

*1-Chloro-4-phenylbutan-2-ol (**3k**).* Colorless oil; 14.8 mg, 40%; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.31−7.28 (m, 2H), 7.22−7.21 (m, 3H), 3.84−3.80 (m, 1H), 3.63 (dd, J = 3.2, 11.2 Hz, 1H), 3.50 (dd, J = 7.2, 11.2 Hz, 1H), 2.87−2.81 (m, 1H), 2.75−2.69 (m, 1H), 2.20 (d, J = 2.9 Hz, 1H), 1.90−1.82 ppm (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 141.3, 128.5, 128.4, 126.0, 70.6, 50.5, 35.8, 31.7 ppm; IR ($CHCl_3$): 3586, 3064, 1603, 1497, 1265 cm^{-1}; HRMS (ESI$^+$-TOF): Calcd for $[C_{10}H_{13}ClO + H]^+$: m/z = 185.0728, Found: 185.0727.

Typical Procedure for Dichlorination. To a solution of **1** (124 mg, 0.44 mmol) and 4-phenylpyridine N-oxide (34 mg, 0.2 mmol) in 1,2-dichloroethane (4 mL) was added 4-methoxystyrene **2a** (26 μL, 0.2 mmol) at 40 °C. The mixture was stirred for 24 h at the same temperature, then passed through a short pad of silica gel, and the silica gel was washed with CH_2Cl_2. The organic solvent was concentrated under reduced pressure. The residue was purified by a recycle GPC system ($CHCl_3$) to provide **4a** (32.7 mg, 80%).

*1-(1,2-Dichloroethyl)-4-methoxybenzene (**4a**).* Yellowish viscous oil; 32.7 mg, 80%; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.33 (d, J = 9.1 Hz, 2H), 6.91 (d, J = 9.1 Hz, 2H), 4.98 (dd, J = 6.2, 8.4 Hz, 1H), 3.99 (dd, J = 6.2, 11.3 Hz, 1H), 3.91 (dd, J = 8.4, 11.3 Hz, 1H), 3.82 ppm (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 160.1, 130.1, 128.7, 114.2, 61.6, 55.3, 48.3 ppm; IR ($CHCl_3$): 3005, 1612, 1516, 1254 cm^{-1}; HRMS (ESI$^+$-TOF): Calcd for $[C_9H_{10}Cl_2O + Na]^+$: m/z = 227.0006, Found: 226.9988.

*5-(1,2-Dichloroethyl)benzo[d][1,3]dioxole (**4b**).* Colorless oil; 30.3 mg, 69%; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.90 (d, J = 1.7, 1H), 6.86 (dd, J = 1.7, 7.9 Hz, 1H), 6.79 (d, J = 7.9, 1H), 5.99 (s, 2H) 4.30 (dd, J = 6.5, 8.4 Hz, 1H), 3.96 (dd, J = 6.5, 11.2 Hz, 1H), 3.87 ppm (dd, J = 8.4, 11.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 148.3, 148.1, 131.7, 121.6, 108.2, 107.3, 101.5, 61.8, 48.3 ppm; IR ($CHCl_3$): 3036, 3009, 1492, 1446, 1238 cm^{-1}; HRMS (ESI$^+$-TOF): Calcd for $[C_9H_8Cl_2O_2 + H]^+$: m/z = 218.9974, Found: 218.9976.

*1-Chloro-4-(1,2-dichloroethyl)benzene (**4d**).* Colorless oil; 14.2 mg, 34%; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.39−7.34 (m, 4H), 4.97 (dd, J = 6.3, 8.3 Hz, 1H), 3.99 (dd, J = 6.3, 11.3 Hz, 1H), 3.88 ppm (dd, J = 8.3, 11.3 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 136.5, 135.0, 129.0, 128.8, 60.6, 48.0 ppm; IR ($CHCl_3$): 3036, 2953, 1495, 1094, 833 cm^{-1}; HRMS (ESI$^+$-TOF): Calcd for $[C_8H_7Cl_3 + H]^+$: m/z = 208.9686, Found: 208.9688.

*1-(1,2-Dichloroethyl)-2-methoxybenzene (**4f**).* Colorless oil; 20.5 mg, 50%; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.47 (dd, J = 1.7, 7.5 Hz, 1H), 7.35−7.31 (m, 1H), 7.01 (ddd, J = 1.2, 7.5, 7.5 Hz, 1H), 6.19 (d, J = 8.0 Hz, 1H), 5.55 (dd, J = 6.7, 7.2 Hz, 1H), 4.03 (dd, J = 6.7, 11.3 Hz, 1H), 3.94 (dd, J = 7.2, 11.3 Hz, 1H), 3.88 ppm (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 156.5, 130.2, 128.3, 126.0, 120.8, 110.9, 56.5, 55.6, 47.9 ppm; IR ($CHCl_3$): 3007, 2960, 1603, 1493, 1265 cm^{-1}; HRMS (ESI$^+$-TOF): Calcd for $[C_9H_{10}Cl_2O - HCl + H]^+$: m/z = 169.0415, Found: 169.0415.

*3,4-Dichloro-2,2-dimethylchromane (**4i**).* Yellow solid; 32.2 mg, 70%; Mp 57−58 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.49 (d, J = 7.5 Hz, 1H), 7.22 (dd, J = 1.7, 7.5 Hz, 1H), 7.01−6.98 (m, 1H), 6.83−6.82 (m, 1H), 5.17 (d, J = 8.6 Hz, 1H), 4.23 (d, J = 8.6 Hz, 1H), 1.61 (s, 3H), 1.36 ppm (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 151.9, 130.2, 129.9, 121.5, 120.6, 117.5, 79.0, 67.3, 59.4, 27.6, 19.5 ppm; IR ($CHCl_3$): 3688, 3001, 1605, 1485, 1195 cm^{-1}; HRMS (ESI$^+$-TOF): Calcd for $[C_{11}H_{12}Cl_2O + H]^+$: m/z = 231.0338, Found: 231.0344.

*(3,4-Dichlorobutyl)benzene (**4k**).* Colorless oil; 14.4 mg, 35%; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.33−7.30 (m, 2H), 7.24−7.21 (m, 3H), 4.03−3.98 (m, 1H), 3.78 (dd, J = 5.1, 11.3 Hz, 1H), 3.67 (dd, J = 7.3, 11.3 Hz, 1H), 2.95−2.90 (m, 1H), 2.80−2.74 (m, 1H), 2.35−2.28 (m, 1H), 2.07−2.00 ppm (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 140.4, 128.6, 128.5, 126.3, 60.2, 48.2, 36.7, 32.0 ppm; IR ($CHCl_3$): 3083, 2955, 1603, 1496, 1292 cm^{-1}; HRMS (ESI$^+$-TOF): Calcd for $[C_{10}H_{12}Cl_2 - HCl + H]^+$: m/z = 167.0622, Found: 167.0623.

*1-(4-(tert-Butyl)dimethylsiloxyphenyl)-1,2-dichloroethane (**4l**).* Yellowish oil; 44.7 mg, 73%; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.27 (d, J = 8.5 Hz, 2H), 6.84 (d, J = 8.5 Hz, 2H), 4.97 (dd, J = 6.8, 7.4 Hz, 1H), 3.97 (dd, J = 6.8, 11.3 Hz, 1H), 3.90 (dd, J = 7.4, 11.3 Hz, 1H), 0.99 (s, 9H), 0.22 ppm (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 156.4, 130.7, 128.6, 120.2, 61.8, 48.5, 25.6, 18.2, − 4.4 ppm; IR ($CHCl_3$): 2958, 2932, 2858, 1605, 1512, 1265 cm^{-1}; HRMS (ESI$^+$-TOF): Calcd for $[C_{14}H_{22}Cl_2OSi + H]^+$: m/z = 305.0890, Found: 305.0896.

*tert-Butyl (4-(1,2-dichloroethyl)phenyl)carbamate (**4m**).* Colorless solid; 57.4 mg, 99%; Mp = 123−124 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.39 (d, J = 8.8 Hz, 2H), 7.32 (d, J = 8.8 Hz, 2H), 6.52 (bs, 1H), 4.96 (dd, J = 6.8, 7.9 Hz, 1H), 3.97 (dd, J = 6.8, 11.2 Hz, 1H), 3.89 (dd, J = 7.9, 11.2 Hz, 1H), 1.52 ppm (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 152.5, 139.1, 132.3, 128.2, 118.5, 80.9, 61.5, 48.3, 28.3 ppm; IR ($CHCl_3$): 3687, 3437, 1728, 1523, 1157 cm^{-1}; HRMS (ESI$^+$-TOF): Calcd for $[C_{13}H_{17}Cl_2NO_2 + Na]^+$: m/z = 312.0529, Found: 312.0531.

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Typical Procedure for Azidochlorination. To a solution of **1** (112 mg, 0.4 mmol) and $TMSN_3$ (66 μL, 0.5 mmol) in CH_2Cl_2 (2 mL) was added CsF (60 mg, 0.4 mmol) at 0 °C. Then, 4-methoxystyrene **2a** (26 μL, 0.2 mmol) was added. The mixture was stirred for 12 h at the same temperature and then diluted with ethyl acetate and H_2O. The organic phase was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (*n*-hexane/ethyl acetate = 10/1) to provide **5a** (42.4 mg, quant.).

*1-(1-Azido-2-chloroethyl)-4-methoxybenzene (**5a**).* Yellowish oil; 42.4 mg, quant.; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.26−7.25 (m, 2H), 6.93 (d, *J* = 8.6 Hz, 2H), 4.68 (dd, *J* = 6.9, 6.9 Hz, 1H), 3.82 (s, 3H), 3.67−3.65 ppm (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 160.1, 128.5, 128.3, 114.4, 66.6, 55.3, 47.5 ppm; IR ($CHCl_3$): 3036, 3007, 2110,1611, 1514, 1252 cm^{-1}; HRMS (ESI$^+$-TOF): Calcd for $[C_9H_{10}ClN_3O + H]^+$: *m*/*z* = 212.0585, Found: 212.0589.

*1-(1-Azido-2-chloroethyl)-2-methoxybenzene (**5f**).* Yellowish oil; 8.7 mg, 21%; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.35−7.32 (m, 2H), 7.02−6.99 (m, 1H), 6.92 (d, *J* = 8.0 Hz, 1H), 5.17 (dd, *J* = 4.0, 8.9 Hz, 1H), 3.87 (s, 3H), 3.79 (dd, *J* = 4.0, 11.5 Hz, 1H), 3.64 (dd, *J* = 8.9, 11.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 156.4, 130.0, 127.5, 124.7, 120.9, 110.7, 61.7, 55.5, 46.8 ppm; IR ($CHCl_3$): 3036, 2116, 1493, 1265, 1032 cm^{-1}; HRMS (ESI$^+$-TOF): Calcd for $[C_9H_{10}ClN_3O + Na]^+$: *m*/*z* = 234.0405, Found: 234.0399.

*4-Azido-3-chloro-2,2-dimethylchromane (**5i**).* Colorless oil; 14.3 mg, 30%; *trans*-isomer: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.38 (d, *J* = 7.4 Hz, 1H), 7.25−7.21 (m, 1H), 7.01−6.98 (m, 1H), 6.82 (d, *J* = 8.5 Hz, 1H), 4.61 (d, *J* = 9.4 Hz, 1H), 4.08 (d, *J* = 9.4 Hz, 1H), 1.58 (s, 3H), 1.36 ppm (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 152.2, 130.2, 128.2, 121.4, 119.3, 117.5, 78.6, 65.6, 62.8, 27.4, 19.1 ppm; IR ($CHCl_3$): 2986, 2930, 2106, 1585, 1486, 1240 cm^{-1}; HRMS (ESI$^+$-TOF): Calcd for $[C_{11}H_{12}ClN_3O + H]^+$: *m*/*z* = 238.0742, Found: 238.0745.

*1-(2-Azido-1-chloropropan-2-yl)-4-methoxybenzene (**5j**).* Yellowish oil; 20.9 mg, 46%; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.37 (d, *J* = 8.6 Hz, 2H), 6.92 (d, *J* = 8.6 Hz, 2H), 3.82 (s, 3H), 3.70 (d, *J* = 11.5 Hz, 1H), 3.64 (d, *J* = 11.5 Hz 1H), 1.82 ppm (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.4, 132.5, 127.2, 114.0, 66.0, 55.3, 53.2, 22.4 ppm; IR ($CHCl_3$): 3007, 2114, 1610, 1514, 1253 cm^{-1}; HRMS (ESI$^+$-TOF): Calcd for $[C_{10}H_{12}ClN_3O + Na]^+$: *m*/*z* = 248.0561, Found: 248.0558.

*1-(4-(tert-Butyl)dimethylsiloxyphenyl)-1-azido-2-chloroethane (**5l**).* Yellow viscous oil; 55.8 mg, 89%; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.19 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 4.67 (t, *J* = 7.2 Hz, 1H), 3.66 (d, *J* = 7.2 Hz, 2H), 0.98 (s, 9H), 0.21 ppm (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 156.3, 129.1, 128.1, 120.5, 66.7, 47.6, 25.6, 18.2, −4.4 ppm; IR ($CHCl_3$): 2957, 2930, 2115, 1607, 1521 cm^{-1}; Anal. calcd for $C_{14}H_{22}ClN_3OSi$: C, 53.92; H, 7.11; N, 13.47%. Found: C, 53.54; H, 6.70; N, 13.38%.

*tert-Butyl (4-(1-Azido-2-chloroethyl)phenyl)carbamate (**5m**).* Yellow viscous oil; 37.6 mg, 63%; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.41 (d, *J* = 8.6 Hz, 2H), 7.25 (d, *J* = 8.6 Hz, 2H), 6.57 (brs, 1H), 4.68 (t, *J* = 6.9 Hz, 1H), 3.65 (d, *J* = 6.9 Hz, 2H), 1.52 ppm (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 152.5, 139.1, 130.8, 127.7, 118.7, 80. 9, 66.5, 47.4, 28.3 ppm; IR ($CHCl_3$): 3435, 3036, 2158, 2113, 1728, 1521, 1238 cm^{-1}; HRMS (ESI$^+$-TOF): Calcd for $[C_{13}H_{17}ClN_4O_2 + Na]^+$: *m*/*z* = 319.0932, Found: 319.0932.

Typical Procedure for Chlorothiocyanation. To a solution of **1** (112 mg, 0.4 mmol) in CH_2Cl_2 (2 mL) was added TMSNCS (56 μL, 0.4 mmol) at 0 °C. Then, **2l** (47 mg, 0.2 mmol) was added. The mixture was stirred for 15 min at 0 °C, then diluted with CH_2Cl_2, and the solution was passed through a short pad of silica gel. The solvent was evaporated under reduced pressure. The residue was purified by a recycle GPC system to provide **6l** (50.1 mg, 76%).

*1-(1-Chloro-2-thiocyanatoethyl)-4-methoxybenzene (**6a**).* Yellow oil; 40.3 mg, 88%; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.34 (d, *J* = 8.6 Hz, 2H), 6.93 (d, *J* = 8.6 Hz, 2H), 5.08 (dd, *J* = 7.2, 7.7 Hz, 1H), 3.83 (s, 3H), 3.61 (dd, *J* = 7.2, 13.4 Hz, 1H), 3.46 ppm (dd, *J* = 7.7, 13.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 160.4, 129.6, 128.5, 114.4, 111.1, 60.2, 56.4, 42.0 ppm; IR ($CHCl_3$): 3036, 3007, 2839, 2158, 1610, 1250 cm^{-1}; Anal. calcd for $C_{10}H_{10}ClNOS$: C, 52.75; H, 4.43; N, 6.15%. Found: C, 52.72; H, 4.36; N, 6.21%.

*(1-Chloro-2-thiocyanatoethyl)benzene (**6c**).* Colorless oil; 26.7 mg, 68%; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.43−7.40 (m, 5H), 5.11 (dd, *J* = 7.5, 7.5 Hz, 1H), 3.61 (dd, *J* = 7.5, 13.8 Hz, 1H), 3.48 ppm (dd, *J* = 7.5, 13.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 137.6, 129.6, 129.1, 127.2, 111.0, 60.3, 42.0 ppm; IR ($CHCl_3$): 3036, 3007, 2158, 1492, 1454, 1238, 1196 cm^{-1}; HRMS (ESI$^+$-TOF): Calcd for $[C_9H_8ClNS + H]^+$: *m*/*z* = 198.0139, Found: 198.0131.

*1-Chloro-4-(1-chloro-2-thiocyanatoethyl)benzene (**6d**).* Colorless oil; 27.8 mg, 60%; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.41−7.36 (m, 4H), 5.08 (dd, *J* = 7.2, 7.5 Hz, 1H), 3.60 (dd, *J* = 7.2, 13.5 Hz, 1H), 3.43 ppm (dd, *J* = 7.5, 13.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 136.1, 135.6, 129.4, 128.6, 110.7, 59.4, 41.8 ppm; IR ($CHCl_3$): 3036, 3007, 2160, 1599, 1493, 1238, 1196 cm^{-1}; HRMS (ESI$^+$-TOF): Calcd for $[C_9H_7Cl_2NS + H]^+$: *m*/*z* = 231.9747, Found: 231.9750.

*1-Bromo-4-(1-chloro-2-thiocyanatoethyl)benzene (**6e**).* Yellowish oil; 30.7 mg, 56%; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.56 (d, *J* = 8.6 Hz, 2H), 7.31 (d, *J* = 8.6 Hz, 2H), 5.06 (dd, *J* = 7.5, 7.5 Hz, 1H), 3.59 (dd, *J* = 7.5, 13.8 Hz, 1H), 3.42 ppm (dd, *J* = 7.5, 13.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 136.6, 132.3, 128.8, 123.7, 110.7, 59.5, 41.7 ppm; IR ($CHCl_3$): 3036, 3007, 2160, 1593, 1489, 1196 cm^{-1}; HRMS (ESI$^+$-TOF): Calcd for $[C_9H_7BrClNS + H]^+$: *m*/*z* = 275.9244, Found: 275.9257.

*4-Chloro-2,2-dimethyl-3-thiocyanatochromane (**6i**).* Yellow solid; 99% (NMR yield); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.51 (d, *J* = 8.0 Hz, 1H), 7.27−7.23 (m, 1H), 7.05−7.02 (m, 1H), 6.84−6.82 (dd, *J* = 1.2, 8.6 Hz, 1H), 5.33 (d, *J* = 8.0 Hz, 1H), 3.71 (d, *J* = 8.0 Hz, 1H), 1.68 (s, 3H), 1.42 ppm (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 151.6, 130.6, 130.4, 122.0, 119.8, 117.7, 110.1, 78.4, 60.0, 55.9, 27.9, 21.9 ppm. This compound could not be purified in benzyl chloride form. Thus, isolation was carried out after hydroxylation.

*1-(tert-Butyl)dimethylsiloxyphenyl-1-chloro-2-thiocyanatoethane (**6l**).* Yellowish oil; 50.1 mg, 76%; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.27 (d, *J* = 8.3 Hz, 2H), 6.86 (d, *J* = 8.3 Hz, 2H), 5.06 (dd, *J* = 7.5, 7.5 Hz, 1H), 3.59 (dd, *J* = 7.5, 13.6 Hz, 1H), 3.46 (dd, *J* = 7.5, 13.6 Hz, 1H), 0.98 (s, 9H), 0.21 ppm (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 156.8, 130.3, 128.4, 120.6, 111.1, 60.3, 42.2, 25.6, 18.2, − 4.5 ppm; IR ($CHCl_3$): 3036, 29532, 2858, 1258, 1607, 1173 cm^{-1}; HRMS (ESI$^+$-TOF): Calcd for $[C_{15}H_{22}ClNOSSi + H]^+$: *m*/*z* = 328.0953, Found: 328.0952.

*tert-Butyl (4-(1-Chloro-2-thiocyanatoethyl)phenyl)carbamate (**6m**).* Yellow solid; quant. (NMR yield); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.41 (d, *J* = 8.5, 2H), 7.33 (d, *J* = 8.5 Hz, 2H), 6.56 (bs, 1H), 5.06 (dd, *J* = 7.4, 7.4 Hz, 1H), 3.60 (dd, *J* = 7.4, 13.6 Hz, 1H), 3.45 (dd, *J* = 7.4, 13.6 Hz, 1H), 1.52 ppm (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 152.2, 139.1, 131.5, 128.0, 118.7, 111.0, 81.0, 60.1, 42.0, 28.3 ppm. This compound could not be purified in benzyl chloride form. Thus, isolation was carried out after hydroxylation.

*1-(1-Chloro-2-thiocyanatoethyl)-4-methylbenzene (**6n**).* Yellowish oil; 34.1 mg, 81%; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.30 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 5.08 (dd, *J* = 7.5, 7.5 Hz, 1H), 3.61 (ddd, *J* = 7.5, 13.6 Hz, 1H), 3.47 (ddd, *J* = 7.5, 13.6 Hz, 1H), 2.37 ppm (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 139.7, 134.7, 129.8, 127.0, 111.1, 60.3, 42.0, 21.2 ppm; IR ($CHCl_3$): 3036, 3007, 2158, 1603, 1238, 1196 cm^{-1}; HRMS (ESI$^+$-TOF): Calcd for $[C_{10}H_{10}ClNS + H]^+$: *m*/*z* = 212.0295, Found: 212.0305.

*1-(1-Chloro-2-thiocyanatoethyl)-4-fluorobenzene (**6o**).* Colorless oil; 32.2 mg, 75%; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.44−7.40 (m, 2H), 7.14−7.09 (m, 2H), 5.09 (dd, *J* = 6.9, 8.7 Hz, 1H), 3.60 (dd, *J* = 6.9, 13.8 Hz, 1H), 3.44 ppm (dd, *J* = 8.0, 13.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 163.2 (d, *J* = 249.5 Hz), 133.5 (d, *J* = 3.6 Hz), 129.1 (d, *J* = 9.6 Hz), 116.2 (d, *J* = 21.6 Hz), 110.8, 59.5, 42.0 ppm; IR ($CHCl_3$): 3036, 3007, 2160, 1607, 1512 cm^{-1}; HRMS (ESI$^+$-TOF): Calcd for $[C_9H_7ClFNS + H]^+$: *m*/*z* = 216.0045, Found: 216.0044.

*2-(1-Chloro-2-thiocyanatoethyl)naphthalene (**6p**).* Colorless solid; 35.5 mg, 72%; Mp 64.6−65.4 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.92−9.86 (m, 4H), 7.57−7.50 (m, 3H), 5.28 (dd, *J* = 7.2, 7.7 Hz, 1H), 3.71 (dd, *J* = 7.2, 13.5 Hz, 1H), 3.57 ppm (dd, *J* = 7.7, 13.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 134.7, 133.6,

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132.9, 129.4, 128.2, 127.8, 127.2, 127.1, 127.0, 123.6, 110.0, 60.6, 41.8 ppm; IR ($CHCl_3$): 3036, 3007, 2158, 1601, 1510, 1238, 1196 cm^{-1}; HRMS (ESI$^+$-TOF): Calcd for $[C_{13}H_{10}ClNS - HCl + H]^+$: m/z = 212.0528, Found: 212.0527.

Typical Procedure for Oxythiocyanation. To a solution of **1** (112 mg, 0.4 mmol) in CH_2Cl_2 (2 mL) was added TMSNCS (56 μL, 0.4 mmol) at 0 °C. Then, **2m** (44 mg, 0.2 mmol) was added. The mixture was stirred for 15 min at 0 °C, then diluted with CH_2Cl_2, and the solution was passed through a short pad of silica gel. The solvent was evaporated under reduced pressure. The residue was dissolved in acetone/H_2O. The solution was stirred for 15 min at room temperature and then extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by chromatography on silica gel (*n*-hexane/ethyl acetate = 10/1) to give **7m** (44.7 mg, 76%).

*2,2-Dimethyl-3-thiocyanatochroman-4-ol (**7i**).* Yellow solid; 29.1 mg, 62%; Mp 62−65 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.49 (d, J = 7.5 Hz, 1H), 7.26−7.23 (m, 1H), 7.20 (dd, J = 7.5, 7.5 Hz, 1H), 6.28 (d, J = 9.2 Hz, 1H), 4.92 (d, J = 9.2 Hz, 1H), 3.42 (d, J = 9.2 Hz, 1H), 1.64 (s, 3H), 1.39 ppm (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 151.6, 130.1, 128.0, 122.4, 121.6, 117.2, 110.9, 78.7, 67.4, 59.7, 28.0, 21.0 ppm; IR ($CHCl_3$): 3595, 3036, 2990, 2156, 1610, 1585, 1485, 1456 cm^{-1}; HRMS (ESI$^+$-TOF): Calcd for $[C_{12}H_{13}NO_2S + H]^+$: m/z = 236.0740, Found: 236.0738.

*tert-Butyl (4-(1-Hydroxy-2-thiocyanatoethyl)phenyl)carbamate (**7m**).* Yellow solid; 44.7 mg, 76%; Mp 102−106 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.38 (d, J = 8.6 Hz, 2H), 7.30 (d, J = 8.6 Hz, 2H), 6.55 (brs, 1H), 4.97 (dd, J = 4.0, 8.6 Hz, 1H), 3.22 (dd, J = 4.0, 13.2 Hz, 1H), 3.15 (dd, J = 8.6, 13.2 Hz, 1H) 1.52 ppm (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 152.6, 138.8, 135.1, 126.6, 118.8, 112.3, 80.9, 72.3, 41.9, 28.3 ppm; IR ($CHCl_3$): 3036, 3007, 1726, 1521, 1238 cm^{-1}; HRMS (ESI$^+$-TOF): Calcd for $[C_{14}H_{18}N_2O_3S + Na]^+$: m/z = 317.0930, Found: 317.0937.

Typical Procedure for Iodoesterification. To a solution of **1** (85 mg, 0.3 mmol) in CH_2Cl_2 (1 mL) was added TBIA (111 mg, 0.3 mmol) at room temperature. Then, 4-methoxystyrene **2a** (26 μL, 0.2 mmol) was added. The mixture was warmed up to 40 °C, stirred for 6 h, and then diluted with ethyl acetate and H_2O. The organic phase was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (*n*-hexane/ethyl acetate = 10/1) to provide **8a** (84.3 mg, 83%).

*2-Iodo-1-(4-methoxyphenyl)ethyl 2-Iodobenzoate (**8a**).* Yellowish oil; 84.3 mg, 83%; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.00 (dd, J = 1.1, 7.9 Hz, 1H), 7.92 (dd, J = 1.7, 7.9 Hz, 1H), 7.44−7.41 (m, 1H), 7.38 (d, J = 8.8 Hz, 2H), 7.16 (ddd, J = 1.7, 7.9, 7.9 Hz, 1H), 6.91 (d, J = 8.8 Hz, 2H), 6.09 (dd, J = 5.7, 7.9 Hz, 1H), 3.81 (s, 3H), 3.66 (dd, J = 7.9, 10.6 Hz, 1H), 3.56 ppm (dd, J = 5.7, 10.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.0, 160.0, 141.4, 134.5, 132.8, 131.3, 130.0, 128.1, 127.9, 114.1, 94.3, 76.4, 55.3, 7.6 ppm; IR ($CHCl_3$): 3007, 1730, 1514, 1254 cm^{-1}; HRMS (ESI$^+$-TOF): Calcd for $[C_{16}H_{14}I_2O_3 + Na]^+$: m/z = 530.8925, Found: 530.8932.

*1-(Benzo[d][1,3]dioxol-5-yl)-2-iodoethyl 2-Iodobenzoate (**8b**).* Colorless oil; 103.4 mg, 99%; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.01 (d, J = 8.6 Hz, 1H), 7.93 (dd, J = 1.7, 8.0 Hz, 1H), 7.45−7.42 (m, 1H), 7.19−7.16 (m, 1H), 6.94−6.92 (m, 2H), 6.81 (d, J = 8.0 Hz, 1H), 6.03 (dd, J = 5.7, 7.5 Hz, 1H), 5.98 (s, 2H), 3.63 (dd, J = 7.5, 10.6 Hz, 1H), 3.54 ppm (dd, J = 5.7, 10.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 164.9, 148.0, 147.9, 141.5, 134.2, 133.0, 131.8, 131.3, 128.0, 120.8, 108.4, 106.9, 101.3, 94.4, 76.5, 7.5 ppm; IR ($CHCl_3$): 3007, 1732, 1489, 1250, 810 cm^{-1}; HRMS (ESI$^+$-TOF): Calcd for $[C_{16}H_{12}I_2O_4 + Na]^+$: m/z = 544.8717, Found: 544.8728.

*2-Iodo-1-phenylethyl 2-Iodobenzoate (**8c**).* Colorless oil; 47.6 mg, 50%; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.01 (d, J = 8.0 Hz, 1H), 7.96 (dd, J = 1.7, 7.5 Hz, 1H), 7.46−7.35 (m, 6H), 7.19−7.16 (m, 1H), 6.12 (dd, J = 5.2, 7.5 Hz, 1H), 3.66, (dd, J = 7.5, 10.6 Hz, 1H), 3.60 ppm (dd, J = 5.2, 10.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.0, 141.5, 138.0, 134.3, 132.9, 131.3, 128.9, 128.7, 128.0, 126.6, 94.4, 76.5, 7.5 ppm; IR ($CHCl_3$): 3022, 1732, 1242, 1132, 1099 cm^{-1}; HRMS (ESI$^+$-TOF): Calcd for $[C_{15}H_{12}I_2O_2 + Na]^+$: m/z = 500.8819, Found: 500.8833.

*2-Iodo-1-(2-methoxyphenyl)ethyl 2-Iodobenzoate (**8f**).* Colorless oil; 94.5 mg, 93%; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.05 (dd, J = 1.7, 7.9 Hz, 1H), 8.02 (d, J = 7.9 Hz, 1H), 7.46 (ddd, J = 1.1, 7.4, 7.9 Hz, 1H), 7.41 (dd, J = 1.1, 7.7 Hz, 1H), 7.34−7.30 (m, 1H), 7.19 (ddd, J = 1.7, 7.4, 7.9 Hz, 1H), 6.98−6.95 (m, 1H), 6.91 (d, J = 8.5 Hz, 1H), 6.44 (dd, J = 4.0, 7.4 Hz, 1H), 3.89 (s, 3H), 3.73 (dd, J = 4.0, 10.5 Hz, 1H), 3.58 ppm (dd, J = 7.4, 10.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 164.8, 156.1, 141.5, 134.4, 132.9, 131.4, 129.6, 128.0, 126.6, 120.6, 110.6, 94.4, 71.3, 55.5, 7.8 ppm; IR ($CHCl_3$): 3009, 1732, 1493, 1242, 1103 cm^{-1}; HRMS (ESI$^+$-TOF): Calcd for $[C_{16}H_{14}I_2O_3 + Na]^+$: m/z = 530.8925, Found: 530.8926.

*3-Iodo-2,2-dimethylchroman-4-yl 2-Iodobenzoate (**8i**).* Yellow solid; 59.8 mg, 56%; Mp 94−96 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.04 (d, J = 7.9 Hz, 1H), 7.87 (dd, J = 1.7, 7.9 Hz, 1H), 7.43−7.39 (m, 1H), 7.29−7.24 (m, 2H), 7.19 (ddd, J = 1.7, 7.4, 7.9 Hz, 1H), 6.94 (dd, J = 7.4, 7.4 Hz, 1H), 6.87 (d, J = 7.9 Hz, 1H), 6.66 (d, J = 7.7 Hz, 1H), 4.61 (d, J = 7.7 Hz, 1H), 1.70 (s, 3H), 1.60 ppm (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.0, 152.9, 141.5, 134.3, 133.0, 131.1, 130.3, 128.6, 128.0, 121.2, 118.6, 117.5, 94.6, 78.3, 73.9, 36.6, 28.4, 24.3 ppm; IR ($CHCl_3$): 3035, 3007, 1730, 1585, 1246, 1196 cm^{-1}; HRMS (ESI$^+$-TOF): Calcd for $[C_{18}H_{16}I_2O_3 + Na]^+$: m/z = 556.9081, Found: 556.9091.

*1-Iodo-2-(4-methoxyphenyl)propan-2-yl 2-Iodobenzoate (**8j**).* Colorless oil; 103.4 mg, 99%; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.00−7.95 (m, 2H), 7.46−7.42 (m, 1H), 7.37 (d, J = 8.9 Hz, 2H), 7.17 (ddd, J = 1.7, 7.5, 7.5 Hz, 1H), 6.90 (d, J = 8.9 Hz, 2H), 3.93 (d, J = 10.3 Hz, 1H), 3.84 (d, J = 10.3 Hz, 1H), 3.81 (s, 3H), 2.14 ppm (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 164.7, 159.1, 141.3, 135.6, 133.3, 132.6, 131.2, 128.0, 126.2, 113.9, 93.9, 82.5, 55.3, 25.8, 17.5 ppm; IR ($CHCl_3$): 3007, 1730, 1514, 1292, 1252 cm^{-1}; HRMS (ESI$^+$-TOF): Calcd for $[C_{17}H_{16}I_2O_3 + Na]^+$: m/z = 544.9081, Found: 544.9089.

*2-(4-(tert-Butyl)dimethylsiloxyphenyl)-1-iodoethyl-2-yl 2-Iodobenzoate (**8l**).* Colorless oil; 56.9 mg, 47%; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.00 (dd, J = 7.9 Hz, 1H), 7.93 (dd, J = 1.7, 7.9 Hz, 1H), 7.44−7.41 (m, 1H), 7.32 (d, J = 8.5 Hz, 2H), 7.16 (ddd, J = 1.7, 7.4, 7.9 Hz, 1H), 6.84 (d, J = 8.5 Hz, 2H), 6.09 (dd, J = 5.1, 7.9, 1H), 3.65 (dd, J = 7.9, 10.6 Hz, 1H), 3.56 (dd, J = 5.1, 10.6 Hz, 1H), 0.98 (s, 9H), 0.20 ppm (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.0, 156.2, 141.4, 134.5, 132.8, 131.2, 130.6, 128.0, 127.9, 120.2, 94.3, 76.4, 25.6, 18.2, 7.7, − 4.4 ppm; IR ($CHCl_3$): 3007, 2957, 2932, 1730, 1510, 1265 cm^{-1}; HRMS (ESI$^+$-TOF): Calcd for $[C_{21}H_{26}I_2O_3Si + Na]^+$: m/z = 630.9633, Found: 630.9632.

*1-(4-((tert-Butoxycarbonyl)amino)phenyl)-2-iodoethyl 2-Iodobenzoate (**8m**).* Yellowish solid; 63.2 mg, 53%; Mp 116−117 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.99 (d, J = 7.9 Hz, 1H), 7.92 (dd, J = 1.7, 7.4 Hz, 1H), 7.44−7.36 (m, 5H), 7.18−7.15 (m, 1H), 6.54 (bs, 1H), 6.07 (dd, J = 5.7, 7.9, 1H), 3.64 (dd, J = 7.9, 10.8 Hz, 1H), 3.55 (dd, J = 5.7, 10.8 Hz, 1H), 1.51 ppm (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.0, 152.6, 141.5, 139.0, 134.4, 132.9, 132.4, 131.3, 128.0, 127.5, 118.5, 94.3, 80.8, 76.3, 28.3, 7.4 ppm; IR ($CHCl_3$): 3437, 3035, 3007, 1728, 1517, 1254, 1159 cm^{-1}; HRMS (ESI$^+$-TOF): Calcd for $[C_{20}H_{21}I_2NO_4 + Na]^+$: m/z = 615.9452, Found: 615.9442.

Typical Procedure for Site-Selective Oxychlorination. To a solution of **1** (62 mg, 0.22 mmol) in acetone/H_2O (2 mL/2 mL) was added **2q** (32 mg, 0.2 mmol) at 40 °C. The solution was stirred for 24 h at the same temperature, then quenched with sat. $NaHCO_3$, and diluted with ethyl acetate and H_2O. The organic phase was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (*n*-hexane/ethyl acetate = 10/1) to provide **3q** (23.1 mg, 54%).

*1-(4-(Allyloxy)phenyl)-2-chloroethan-1-ol (**3q**).* Colorless solid; 23.1 mg, 54%; Mp 49−51 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.30 (d, J = 8.8 Hz, 2H), 6.92 (d, J = 8.8 Hz, 2H), 6.09−6.01 (m, 1H), 5.41 (dd, J = 1.7, 17.6 Hz, 1H), 5.29 (dd, J = 1.7, 10.5 Hz, 1H), 4.86−4.84 (m, 1H), 4.55−4.53, (m, 2H), 3.71 (dd, J = 3.7, 11.2 Hz, 1H), 3.63 (dd, J = 8.5, 11.2 Hz, 1H), 2.59 ppm (d, J = 2.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.7, 133.1, 132.2, 127.3, 117.8, 114.9, 73.7, 68.8, 50.9 ppm; IR ($CHCl_3$): 3036, 3007, 1610, 1512, 1238, 1196

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cm^{-1}; HRMS (ESI$^+$-TOF): Calcd for $[C_{11}H_{13}ClO_2 + Na]^+$: m/z = 235.0496, Found: 235.0495.

*2-Chloro-1-(2,2-dimethyl-2H-chromen-6-yl)ethan-1-ol (**3r**).* Colorless oil; 28.5 mg, 60%; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.10 (dd, J = 1.7, 8.0 Hz, 1H), 7.01 (d, J = 1.7 Hz, 1H), 6.76 (d, J = 8.0 Hz, 1H), 6.31 (d, J = 10.0 Hz, 1H), 5.63 (d, J = 10.0 Hz, 1H), 4.81−4.79 (m, 1H), 3.70 (dd, J = 3.4, 11.3 Hz, 1H), 3.62 (dd, J = 9.4, 11.3 Hz, 1H), 2.56 (d, J = 2.3 Hz, 1H), 1.43 ppm (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.1, 132.0, 131.2, 126.8, 124.0, 122.0, 121.4, 116.4, 76.5, 73.8, 51.0, 28.0, 28.0 ppm; IR ($CHCl_3$): 3595, 3007, 1639, 1491, 1263 cm^{-1}; HRMS (ESI$^+$-TOF): Calcd for $[C_{13}H_{15}ClO_2 + Na]^+$: m/z = 261.0653, Found: 261.0641.

Typical Procedure for Site-Selective Dichlorination. To a solution of **1** (124 mg, 0.44 mmol) and 4-phenylpyridine *N*-oxide (34 mg, 0.2 mmol) in 1,2-dichloroethane (4 mL) was added **2q** (32 mg, 0.2 mmol) at 40 °C. The mixture was stirred for 24 h at the same temperature, then passed through a short pad of silica gel, and the silica gel was washed with CH_2Cl_2. The organic solvent was evaporated under reduced pressure. The residue was purified by recycle GPC system ($CHCl_3$) to provide **4q** (31.7 mg, 69%).

*1-(Allyloxy)-4-(1,2-dichloroethyl)benzene (**4q**).* Colorless oil; 31.7 mg, 69%; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.32 (d, J = 8.6 Hz, 2H), 6.92 (d, J = 8.6 Hz, 2H), 6.09−6.01 (m, 1H), 5.42 (dd, J = 1.7, 17.2, 1H), 5.30 (dd, J = 1.7, 10.3 Hz, 1H), 4.98 (dd, J = 6.3, 8.0 Hz, 1H), 4.55 (d, J = 5.2 Hz, 2H), 3.99 (dd, J = 6.3, 11.5 Hz, 1H), 3.91 ppm (dd, J = 8.0, 11.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.1, 132.9, 130.2, 128.7, 117.9, 114.9, 68.8, 61.6, 48.3 ppm; IR ($CHCl_3$): 1611, 1512, 1242, 1178, 835 cm^{-1}; HRMS (ESI$^+$-TOF): Calcd for $[C_{11}H_{12}Cl_2O + H]^+$: m/z = 231.0338, Found: 231.0344.

*6-(1,2-Dichloroethyl)-2,2-dimethyl-2H-chromene (**4r**).* Yellowish oil; 32.5 mg, 63%; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.12 (dd, J = 2.3, 8.2 Hz, 1H), 7.00 (d, J = 2.3 Hz, 1H), 6.76 (d, J = 8.2 Hz, 1H), 6.30 (d, J = 9.9 Hz, 1H), 5.64 (d, J = 9.9 Hz, 1H), 4.92 (dd, J = 6.8, 7.9 Hz, 1H), 3.96 (dd, J = 6.8, 11.2 Hz, 1H), 3.89 (dd, J = 7.9, 11.2 Hz, 1H), 1.44 ppm (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.6, 131.3, 130.1, 128.1, 125.3, 121.8, 121.3, 116.5, 61.9, 48.4, 28.2 ppm; IR ($CHCl_3$): 3035, 2978, 1730, 1610, 1491, 1238, 1195 cm^{-1}; HRMS (ESI$^+$-TOF): Calcd for $[C_{13}H_{14}Cl_2O + Na]^+$: m/z = 279.0314, Found: 279.0320.

Typical Procedure for Site-Selective Iodoesterification. To a solution of **1** (85 mg, 0.3 mmol) in $CHCl_3$ (1 mL) was added TBIA (111 mg, 0.3 mmol) at room temperature. Then, **2q** (32 mg, 0.2 mmol) was added. The mixture was warmed up to 40 °C, stirred for 3 h, and diluted with ethyl acetate and H_2O. The organic phase was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (*n*-hexane/ethyl acetate = 10/1) to provide **8q** (69.1 mg, 65%).

*1-(4-(Allyloxy)phenyl)-2-iodoethyl 2-Iodobenzoate (**8q**).* Yellowish oil; 69.1 mg, 65%; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.00 (d, J = 7.5 Hz, 1H), 7.92 (dd, J = 1.7, 8.0 Hz, 1H), 7.44−7.36 (m, 3H), 7.17 (ddd, J = 1.7, 7.5, 7.5 Hz, 1H), 6.92 (d, J = 8.6 Hz, 2H), 6.10−6.01 (m, 2H), 5.41 (dd, J = 1.7, 17.2 Hz, 1H), 5.29 (dd, J = 1.7, 10.6 Hz, 1H), 3.65 (dd, J = 7.7, 10.6 Hz, 1H), 3.56 ppm (dd, J = 5.4, 10.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.0, 159.0, 141.5, 134.4, 133.0, 132.9, 131.3, 130.2, 128.1, 127.9, 117.9, 114.8, 94.3, 76.4, 68.8, 7.6 ppm; IR ($CHCl_3$): 3035, 1730, 1611, 1512, 1240 cm^{-1}; HRMS (ESI$^+$-TOF): Calcd for $[C_{18}H_{16}I_2O_3 + Na]^+$: m/z = 556.9081, Found: 556.9087.

*1-(Benzo[d][1,3]dioxol-5-yl)-2-iodoethyl 2-Iodobenzoate (**8r**).* Colorless oil; 59.5 mg, 58%; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.00 (d, J = 7.5 Hz, 1H), 7.93 (dd, J = 1.7, 8.0 Hz, 1H), 7.43 (dd, J = 7.5, 7.5 Hz, 1H), 7.19−7.15 (m, 2H), 7.05 (d, J = 2.3 Hz, 1H), 6.77 (d, J = 8.0 Hz, 1H), 6.31 (d, J = 10.0 Hz, 1H), 6.04 (dd, J = 5.2, 8.0 Hz, 1H), 5.63 (d, J = 10.0 Hz, 1H), 3.64 (dd, J = 8.0, 10.7 Hz, 1H), 3.54 ppm (dd, J = 5.2, 10.7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.0, 153.4, 141.5, 134.4, 132.8, 131.3, 131.2, 130.1, 127.9, 127.4, 124.9, 121.9, 121.2, 116.5, 94.3, 76.6, 76.5, 28.1, 7.6 ppm; IR ($CHCl_3$): 2797, 1730, 1491, 1250, 1126, 909 cm^{-1}; HRMS (ESI$^+$-TOF): Calcd for $[C_{20}H_{18}I_2O_3 + Na]^+$: m/z = 582.9238, Found: 582.9219.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00295.

Optimization of the reaction conditions and NMR spectra of isolated products (PDF)

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Notes

The authors declare no competing financial interest.

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