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Studies on the Intermolecular Hydroarylation of *N*-Ts- or *N*-Ac-Protected Indoles and 2,3-Allenoates

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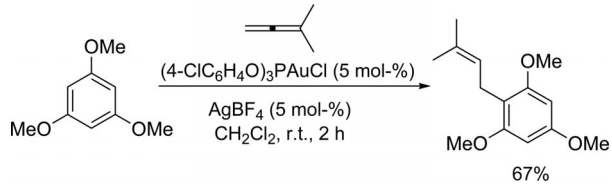
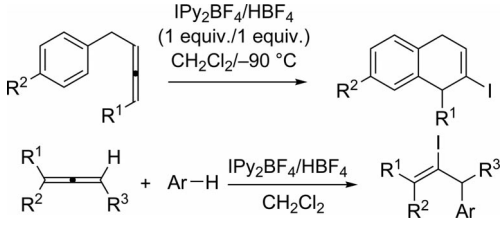
An operationally simple, TFA-promoted regioselective hydroarylation reaction of 2,3-allenoates with *N*-Ts- or *N*-Ac-indoles to afford 4-indolyl-4-arylbut-2-enoates is described. A series of substrates was tested, and the *E*/*Z* selectivity was found to depend on the reaction temperature and time. A mechanism involving the formation of *E* and *Z* allylic carbocations generated in situ from the reaction of 2,3-allenoate with TFA and subsequent Friedel–Crafts attack at the 3-position of the indoles was proposed to explain the results.

Introduction

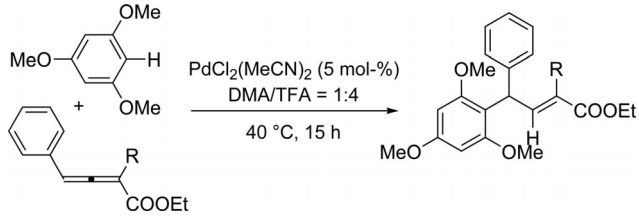
The direct addition of arenes to unactivated multiple bonds such as alkenes, alkynes, and allenes commonly referred to as the hydroarylation reaction represents an attractive tool for the construction of new C–C bonds.[1,2] Among these transformations, the reactions of functionalized allenes are especially interesting due to regio- and stereoselectivity control and the structural complexity of the products.[3] As an intramolecular version, Widenhoefer et al. reported an efficient reaction of 3,4-allenoates with an indole nucleophile to construct cyclic compounds with exclusive 6-*exo* selectivity and complete transfer of axial chirality to the newly formed stereocenter,[3a] whereas Nelson et al. applied a gold-catalyzed annulation of enantioenriched allene with pyrrole to the total synthesis of (–)-rhazinilam.[3b] In addition, Ohno et al. achieved the hydroarylation of *N*-(1,2-allenyl)anilines and phenols to afford dihydroquinoline and chromene derivatives.[3c] Intermolecular hydroarylations of allenes, though relatively rare, were also developed recently: In 2009, Gagné found that unsubstituted 3-methylbuta-1,2-diene reacted with electron-rich arenes such as 1,3,5-trimethoxybenzene to form differently substituted allylbenzene (Scheme 1).[3k] Unfortunately, these reactions could not be advanced with heterocyclic rings such as indoles, furans, and pyrroles. In the absence of precious metal catalysts, in 2009, Barluenga observed an interesting iodoarylation of allenes in both intra- and intermolecular processes in which the iodine, like the gold or platinum catalyst in other cases, served as the π-acidic reagent (Scheme 2).[4a] Recently, we have reported a $[PdCl_2(MeCN)_2]$-catalyzed highly regio- and stereoselective allylation of electron-rich arenes with 2,3-allenoates, in which less electron-rich substrates such as phenol and anisole may also be applied (Scheme 3).[3l]



Scheme 1. Gold(I)-catalyzed intermolecular hydroarylation of allenes with electron-rich arenes.



Scheme 2. Intra- and intermolecular iodoarylation of allenes.



Scheme 3. Pd-catalyzed hydroarylation of 2,3-allenoate with electron-rich arenes.

On the other hand, indole derivatives are important building blocks and common structural units in organic synthesis.[1h,5] The two C–H bonds at the C-2 and C-3 position of indole may be functionalized at these two sites in

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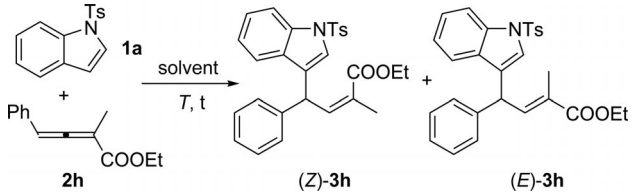
many chemical transformations.[6–8] However, *N*-acetyl- and *N*-tosyl-protected indoles are usually inactive because of the electron-withdrawing nature of these groups. Herein, we wish to disclose our observation on a trifluoroacetic acid (TFA)-promoted Friedel–Crafts allylation of acetyl- and tosyl-protected indoles to afford 4-indolyl-4-arylbut-2-enoates in moderate to good yields with reasonable control over the *E*/*Z* selectivity.

Results and Discussion

Because of the decomposition of unprotected indole in TFA, the hydroarylation of 2,3-allenoates was tested on the reaction with the relatively electron-deficient *N*-tosylindole **1a** (traditionally regarded as inactive for such reactions) with ethyl 2-methyl-4-phenylbuta-2,3-dienoate (**2h**). As a first try, the reaction in a mixture of CH_3NO_2 and TFA afforded a mixture of (*Z*)-**3h** in 47% yield and (*E*)-**3h** in 9% yield (determined by NMR spectroscopy), which could be separated easily by chromatography on silica gel (Table 1, Entry 1). The yields and selectivity varied as the co-solvent was changed, whereas pure TFA gave the best result (Table 1, Entry 5). Different from previous reported,[31] addition of palladium catalysts slightly decreased the yield and changed the selectivity as well (Table 1, Entries 6–8). A lower reaction temperature obviously improved the selectivity and had a limited impact on the yield, as the *Z*/*E* mixture was obtained with a selectivity of 94:6 (Table 1, En-

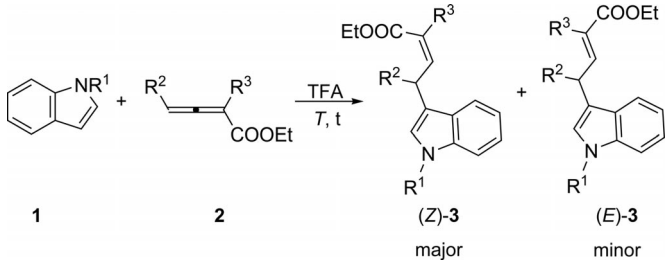
Table 1. Optimization of reaction conditions for the hydroarylation of *N*-tosylindole **1a** with **2h**.[a]



Entry	Solvent	Additive	*T* [°C]	*t* [h]	Yield of main product [%]	*Z*/*E*
1	CH_3NO_2/TFA	–	40	8.5	47 (44)[b]	84:16
2	CH_3CN/TFA	–	40	10	59	91:9
3	DMA/TFA	–	40	48	38[c]	90:10
4	DCM/TFA	–	40	2.5	69	92:8
5	TFA	–	40	2.5	69 (66)	92:8
6	TFA	$Pd(OAc)_2$	40	6	52[d]	90:10
7	TFA	$PdCl_2(MeCN)_2$	40	6	59[e]	95:5
8	TFA	$PdCl_2(PPh_3)_3$	40	6	61[f]	90:10
9	TFA	–	10	13	64 (64)	94:6
10	TFA	–	60	24	47 (51)	13:87
11	TFA	–	80	11	54 (58)	4:96

[a] The reaction was carried out by using **1a** (0.3 mmol) and **2h** (1.2 equiv.) in TFA (1.2 mL) and co-solvent (0.3 mL) or TFA (1.5 mL). The yields and selectivities were determined by ^{1}H NMR spectroscopic analysis with CH_2Br_2 as the internal standard. [b] Isolated yield. [c] *N*-Tosylindole **1a** was recovered in 31%. [d] *N*-Tosylindole **1a** was recovered in 9%. [e] *N*-Tosylindole **1a** was recovered in 9%. [f] *N*-Tosylindole **1a** was recovered in 3%.

Table 2. Reactions of different 2,3-allenoates with *N*-Ts- and *N*-Ac-protected indoles **1**.[a]



Entry	R^1	R^2	R^3	*T* [°C]	*t* [h]	*Z*/*E* of **3**	Isolated yield of (*Z*)-**3** [%]
1	Ts (**1a**)	4-FC_6H_4	Me (**2a**)	28	12	89:11	71 [(*Z*)-**3a**]
2	Ts (**1a**)	4-ClC_6H_4	Me (**2b**)	20	12	94:6	62 [(*Z*)-**3b**]
3	Ts (**1a**)	3-ClC_6H_4	Me (**2c**)	60	12	86:14	48 [(*Z*)-**3c**]
4	Ts (**1a**)	4-BrC_6H_4	Me (**2d**)	40	15	96:4	58 [(*Z*)-**3d**]
5[b]	Ts (**1a**)	4-$MeOC_6H_4$	Me (**2e**)	5	0.5	81:19	68 [(*Z*)-**3e**]
6[b]	Ts (**1a**)	4-MeC_6H_4	Me (**2f**)	–10	5.5	91:9	73 [(*Z*)-**3f**]
7[b]	Ts (**1a**)	α-naphthyl	Me (**2g**)	5	2.5	95:5	78 [(*Z*)-**3g**]
8	Ts (**1a**)	C_6H_5	Me (**2h**)	10	13	94:6	64 [(*Z*)-**3h**]
9[c]	Ts (**1a**)	C_6H_5	Me (**2h**)	10	22	95:5	70 [(*Z*)-**3h**]
10	Ts (**1a**)	C_6H_5	Et (**2i**)	10	24	90:10	59 [(*Z*)-**3i**]
11	Ts (**1a**)	C_6H_5	Allyl (**2j**)	40	15	–[d]	42 [(*Z*)-**3j**]
12	Ts (**1a**)	C_4H_9	Me (**2k**)	60	10	–	–[e]
13	Ac (**1b**)	4-FC_6H_4	Me (**2a**)	20	10	90:10	57 [(*Z*)-**3k**]
14	Ac (**1b**)	C_6H_5	Me (**2h**)	10	15	96:4	61 [(*Z*)-**3l**]

[a] The reaction was carried out by using **1** (0.3 mmol) and **2** (1.2 equiv.) in TFA (1.5 mL), and the selectivities were determined by ^{1}H NMR spectroscopy with CH_2Br_2 as the internal standard. [b] The reaction was carried out using 1.5 equiv. of **2**. [c] The reaction was conducted with **1a** (4 mmol) and **2h** (4.8 mmol). [d] The *E*/*Z* ratio could not be determined by NMR spectroscopy. [e] Indole **1a** was recovered in 45% yield, whereas **2k** decomposed under the reaction conditions.

try 9). Interestingly, a higher temperature and a prolonged reaction time led to the *E* isomer as the main product (Table 1, Entries 10 and 11). When the reaction was conducted at 80 °C, reversed stereoselectivity (4:96) was observed, although a relatively lower yield (54%) was obtained, which is probably due to the in situ decomposition of the 2,3-allenoates. Finally, we defined the reaction in TFA without additives as the standard conditions, and the selectivity was controlled by changing the reaction temperature and time. It should be noted that no Michael addition product was formed under the optimized conditions. This may be explained by the acidic conditions applied.

With the optimized reaction conditions in hand, some typical results of hydroarylation of different 2,3-allenoates with *N*-Ts- or *N*-Ac-protected indoles are summarized in Tables 2 and 3. The reaction proceeded smoothly under standard conditions, affording substituted (*Z*)-**3** as the major products in moderate to good yields (Table 2). When R^1 = tosyl, R^2 could be a phenyl group substituted with either an electron-donating or an electron-withdrawing group. Yields decreased and the selectivity was improved when the *para* substituent was changed from fluorine to bromine (Table 2, Entries 1, 2, and 4). *meta*-Chloro substrate **2c** led to a lower yield because of steric effects (Table 2, Entry 3). Better yields were obtained when R^2 is an electron-rich aryl group (Table 2, Entries 5–7). When R^1 = acetyl, two representative examples showed that the yields range from 57 to 61% (Table 2, Entries 13 and 14). The structure of (*Z*)-**3g** was unambiguously established by X-ray diffraction analysis, indicating the *Z* selectivity and the connecting position of the indolyl group (Figure 1).[9] To our disappointment, if R^2 = alkyl, no reaction occurred at all (Table 2, Entry 12). This reaction can also be conducted on a large scale, which leads to a better yield and selectivity (Table 2, Entry 9).

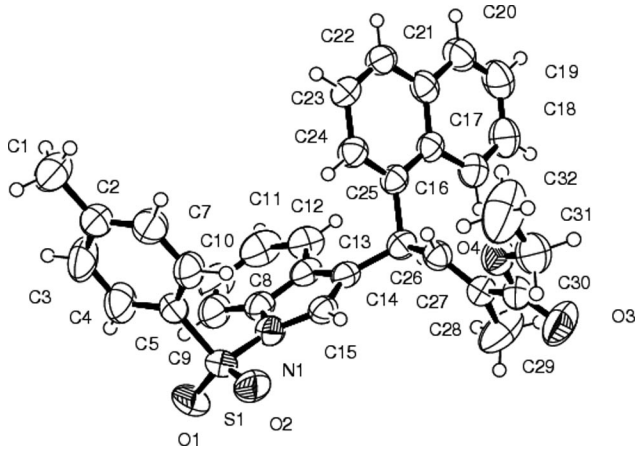


Figure 1. ORTEP representation of *Z*-**3g**.

With a relatively higher temperature and prolonged reaction time, some of these substrates could form the thermodynamically more stable *E* products in moderate yields. Some typical results are listed in Table 3. The structure of (*E*)-**3g** was also unambiguously established by single-crystal X-ray diffraction analysis (Figure 2).[10]

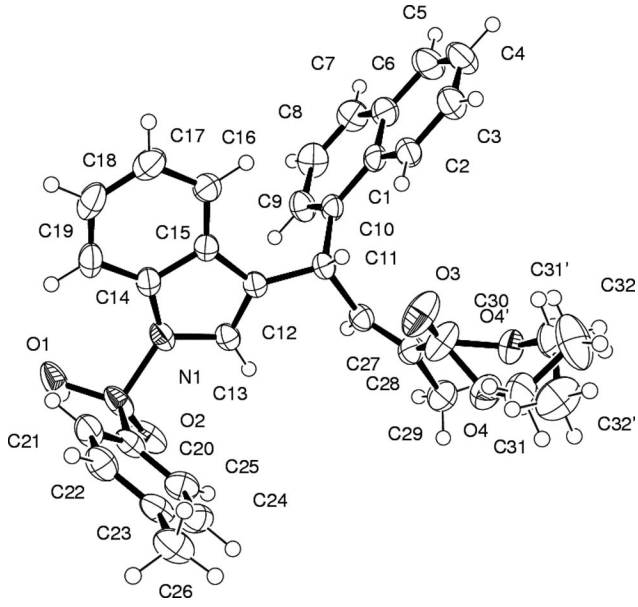
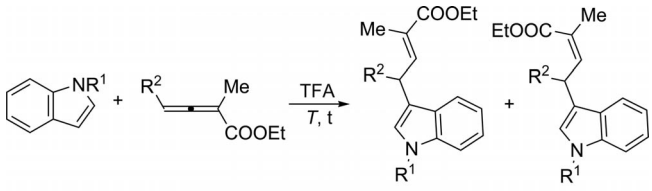


Figure 2. ORTEP representation of (*E*)-**3g**.

Table 3. Reactions of different 2,3-allenoates with *N*-Ts- and *N*-Ac-indoles **1**.[a]



1 **2** (*E*)-**3** major (*Z*)-**3** minor

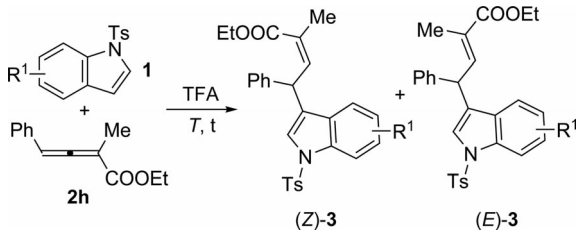
Entry	R^1	R^2	*T* [°C]	*t* [h]	*E*/*Z*	Isolated yield of (*E*)-**3** [%]
1	Ts (**1a**)	4-ClC_6H_4 (**2b**)	60	12	92:8	66 [(*E*)-**3b**]
2[b]	Ts (**1a**)	4-$MeOC_6H_4$ (**2e**)	40	15	98:2	59 [(*E*)-**3e**]
3[b]	Ts (**1a**)	4-MeC_6H_4 (**2f**)	40	12	93:7	65 [(*E*)-**3f**]
4[b]	Ts (**1a**)	α-naphthyl (**2g**)	80	3	78:22	55 [(*E*)-**3g**]
5[c]	Ts (**1a**)	C_6H_5 (**2h**)	80	11	90:10	58 [(*E*)-**3h**]
6[b]	Ac (**1b**)	4-$MeOC_6H_4$ (**2e**)	40	20	88:12	52 [(*E*)-**3m**]

[a] The reaction was carried out by using **1** (0.3 mmol) and **2** (1.2 equiv.) in TFA (1.5 mL), and the selectivities were determined by ^{1}H NMR spectroscopy with CH_2Br_2 as the internal standard. [b] The reaction was carried out by using **2** (1.5 equiv.). [c] *N*-Tosylindole **1a** was recovered in 5%.

Hydroarylation reactions between **2h** and differently substituted *N*-tosylindoles are listed in Table 4. 5-Methylindole (**1c**) is prone to decompose in the acidic reaction mixture probably due to the electron-donating nature of methyl group, thus leading to only moderate yields (Table 4, Entries 1 and 2), as was the case for 5-methoxyindole (**1e**; Table 4, Entry 5). The reaction of 5-bromoindole (**1d**) and the 2,3-allenoate proceeded smoothly at lower temperature (Table 4, Entry 3). However, a higher temperature led to decomposition of the starting material, and as a result, unsat-

isfactory *E*/*Z* selectivity was observed (Table 4, Entry 4). Among these results, it is worth noting that the 5-Br substituent in indole **1d** is well tolerated in this reaction and therefore could be used in further transformations.

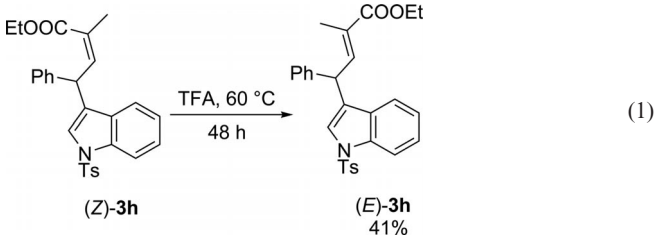
Table 4. Reaction of **2h** with differently substituted indoles.[a]



Entry	R^1	*T* [°C]	*t* [h]	*E*/*Z*	Isolated yield of **3** [%]
1	5-Me (**1c**)	10	11	8:92	58 [(*Z*)-**3n**]
2	5-Me (**1c**)	60	20	96:4	56 [(*E*)-**3n**]
3[b]	5-Br (**1d**)	10	12	7:93	70 [(*Z*)-**3o**]
4[c]	5-Br (**1d**)	60	20	77:23	53 [(*E*)-**3o**]
5	5-OMe (**1e**)	40	12.5	9:91	52 [(*Z*)-**3p**]

[a] The reaction was carried out by using **1** (0.3 mmol) and **2h** (1.2 equiv.) in TFA (1.5 mL), and the selectivities were determined by ^{1}H NMR spectroscopy with CH_2Br_2 as the internal standard. [b] *N*-Tosylindole **1a** was recovered in 6%. [c] *N*-Tosylindole **1a** was recovered in 8%.

On the basis of these results, we concluded that the *Z*/*E* selectivity was controlled by the nature of the 2,3-allenoates, reaction temperature, and reaction time. Protonation of the allene moiety at the center carbon atom afforded the allylic carbocation intermediate. Thus, at lower temperature, the kinetic formation of *Z* allylic carbocation **M1** led to the formation of *Z* products as the major products, whereas a relatively higher temperature and prolonged reaction time led to the formation of the thermodynamically more stable *E* isomer by isomerization. To probe such a possibility, (*Z*)-**3h** was stirred in TFA at 60 °C for 48 h, and just as we expected, (*E*)-**3h** was formed, however, in only 41% yield probably due to the decomposition of **3h** [Equation (1)]. The energy barrier between the two types of carbocations depends on the electronic nature and steric effects of the substituents on the 2,3-allenoates, thus resulting in different selectivity for different substrates (Scheme 4). The aryl group at the 4′-position of the 2,3-allenoates determines the regioselectivity by the stabilizing effects of this aryl group.



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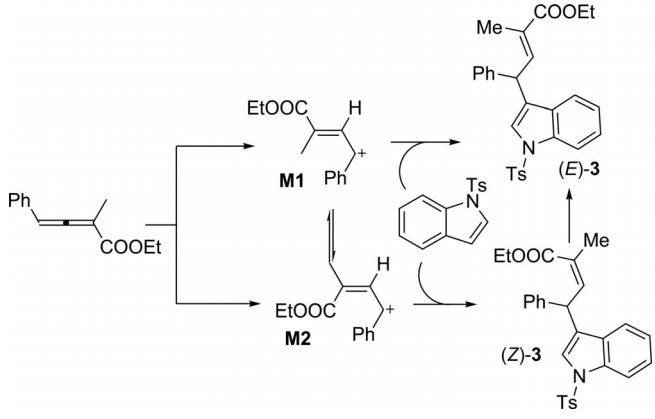

Scheme 4. Proposed mechanism.

Conclusions

In conclusion, we have developed a TFA-promoted regioselective hydroarylation reaction of 2,3-allenoates with *N*-Ts- or *N*-Ac-indoles. Considering the difficulties encountered in the C–H functionalization of *N*-Ts- or *N*-Ac-indoles and the popularity of the indole structure in medicinal and pharmaceutical chemistry,[5] this reaction should be of wide interest. Further study in this area including the application of this reaction in synthesis is being carried out in our laboratory.

Supporting Information (see footnote on the first page of this article): Experimental details; isomerization of (*Z*)-**3h** into (*E*)-**3h**; copies of the ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra of the products.

Acknowledgments

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[9] Crystal data for (*Z*)-**3g**: $C_{32}H_{29}NO_4S$, *Mw* = 523.62, monoclinic, space group $P2_1/c$, final *R* indices [$I>2\sigma(I)$], R_1 = 0.0419, wR_2 = 0.1002, *R* indices (all data) R_1 = 0.0528, wR_2 = 0.1077, *a* = 10.4567(3) Å, *b* = 18.6845(5) Å, *c* = 13.7933(4) Å, α = 90°, β = 96.6330(10)°, γ = 90°, *V* = 2676.87(13) Å^3, *T* = 173(2) K, *Z* = 4, reflections collected/unique: 30728/4712 (R_{int} = 0.0296), number of observations [$I>2\sigma(I)$] 3919, parameters: 370. CCDC-800855 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[10] Crystal data for compound (*E*)-**3g**: $C_{64}H_{58}N_2O_8S_2$, *Mw* = 1047.24, triclinic, space group $P\bar{1}$, final *R* indices [$I>2\sigma(I)$], R_1 = 0.0575, wR_2 = 0.1489, *R* indices (all data) R_1 = 0.0869, wR_2 = 0.1734, *a* = 12.6425(4) Å, *b* = 14.3054(4) Å, *c* = 16.6159(5) Å, α = 104.2780(10)°, β = 94.7360(10)°, γ = 108.6340(10)°, *V* = 2716.65(14) Å^3, *T* = 296(2) K, *Z* = 2, reflections collected/unique: 31870/9496 (R_{int} = 0.0292), number of observations [$I > 2\sigma(I)$] 6526, parameters: 685. CCDC-800854 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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