Rhodium(ii)-catalyzed branch-selective C–H alkylation of aryl sulfonylamides with vinylsilanes†

Supriya Rej and Naoto Chatani DOI: 10.1039/c9sc04308j

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Introduction

The transition metal catalyzed directed C–H activation strategy is one of the most straightforward and site-selective approaches in organic chemistry for constructing C–C bonds. A variety of C–H functionalization reactions have been achieved to date by using a directing group strategy. In particular, directed C–H alkylation with aryl alkenes provides an atom economic protocol because all of the atoms of the starting materials are incorporated into the products. In 1993, Murai reported a ketone-directed strategy for Ru-catalyzed ortho-C–H alkylation of aromatic ketones with alkenes. Following this pioneering reaction, numerous directing groups have been designed for use in regio-selective C–H alkylation reactions. It is noteworthy that most of the reports deal with linear-selective alkylation reactions. However, only a limited number of studies that deal with branch-selective C–H alkylation with aryl alkenes have been reported (Fig. 1A). In this respect, non-directed strategies were discussed for the alkylation of 1,3,4-oxadiazoles (a), indoles (b and c), benzimidazoles (d, e, and j), benzoxazoles (f), benzo-thiazoles (g), pyridines (h), and azines (i) with either styrenes or acrylate esters as coupling partners. A few directed strategies were also demonstrated: Kuninobu and Takai reported a Re-catalyzed branch-selective alkylation of para-substituted phenols (I). Yoshikai reported a Co-catalyzed branched alkylation of 2-arylpyridine with styrene derivatives (II). Ramana reported a Ru-catalyzed ketone-directed C3-alkylation of 2-arylvinazones with α,β-unsaturated carbonyl derivatives (III). Bower reported a carbonyl-directed Ir-catalyzed ortho-alkylation of aromatic ketones (IV). Nishimura reported an Ir-catalyzed alkylation of 2-phenylpyridine derivatives with vinyl ethers (V). Bower reported an Ir-catalyzed branch-selective ortho-alkylation of acetanilides (VI). Hou (VII). In 2017, Ackermann reported a Co-catalyzed branch-selective alkylation of indole using unactivated alkenes with a detailed mechanistic explanation (IX). Yoshikai recently presented a Co-catalyzed N–H imine-directed branch selective alkylation of aromatic imine derivatives with styrenes (X). All of these branch-selective alkylation reactions were achieved using styrenes, acrylate esters, vinyl ethers, and in a few cases unactivated 1-alkenes as coupling partners. However, branch-selective alkylation with vinylsilanes has not been achieved to date, although linear selective alkylation with vinylsilanes with the aid of a directing group strategy has been widely explored (Fig. 1B).

Our group recently reported a series of linear selective C–H alkylations of benzamides, naphthalamides, sulfonylamides, and sulfonylamides with vinyl ketones, acrylate esters, styrenes, N-vinylphthalimides, unactivated 1-alkenes, and vinylsilanes using an 8-aminooquinoline or plicolimamide directing group, which was first introduced by Daugulis in 2005. Having continuous interest in alkylation reactions, we were very interested in achieving a branch selective C–H alkylation. Herein, we report on an unusual branch-selective ortho-C–H alkylation of biologically and medicinally important aryl sulfonylamides with vinylsilanes by taking advantage of an 8-aminooquinoline directing group (Fig. 1C).

Results and discussion

We began our studies by investigating suitable directing groups for the branch-selective alkylation of aryl sulfonylamides with triethylvinylsilane in the presence of a [Rh(OAc)3] catalyst.
The reaction of benzenesulfonamide with triethylvinylsilane in the presence of \([\text{Rh(OAc)}_2]\) and 3-chloro-2-methylbenzoic acid remained unreactive (Table 1). The use of weak coordinating \(N\)-acetyl and \(N\)-phenyl substituted sulfonamides as substrates failed to give the desired product. These observations prompted us to use a strongly coordinating chelation system. However, the use of 2-pyridinylmethylamine and oxazoline-based aniline as directing groups failed to give the desired product. The breakthrough came when 8-aminoquinoline was used as an auxiliary group, giving a 49% yield of the expected product with a decent 92 : 8 branch selectivity (Table 1).

To obtain good yield and selectivity, we continued our optimization studies using \(1a\) as a model substrate and triethylvinylsilane (Table 2). The use of other Rh(i) or Rh(III) catalysts failed to show impressive results (entry 1 vs. entries 2–4). Other acid additives were examined next. Although the use of ortho-toluic acid and pivalic acid slightly improved the product yield, the selectivity decreased (entries 6 and 7). The exact role of an acid additive in the selectivity of the reaction is unclear at this point. Among the carboxylic acid additives examined, 3-chloro-2-methylbenzoic acid was the choice of acid. Finally, we found that the use of 7.5 mol% of Rh(III) catalyst and 2 equiv. of 3-chloro-2-methylbenzoic acid in the reaction of amide \(1a\) and 6 equiv. of triethylvinylsilane at 160 °C for 24 h produced the corresponding branched alkylated product \(2aa\) in 72% isolated yield with a high branch selectivity (86 : 14) (entry 10). Under these optimized conditions, a trace amount of the inseparable alkenylated product \(4aa\) was formed.

With the optimized conditions in hand, the substrate scope was examined for this branch-selective alkylation and the results are shown in Table 3. We observed that \(meta\)-substituted aryl sulfonamides produce the corresponding products in good yield with good selectivity (\(2aa\) and \(2ba\)). A complete site-selectivity for less hindered C–H bonds was found. An \(ortho\)-Me substituted sulfonamide showed moderate reactivity, giving \(2da\) in 46% yield with a selectivity of 88 : 12. Most importantly, when \(para\)-substituted aryl sulfonamides were used, the corresponding branched alkylated products were obtained in good yields with excellent branch-selectivity over 90 : 10 (\(2ca\) and \(2ea-ma\)). Importantly, this branch selective alkylation reaction is well tolerable for various functional groups such as \(-\text{OMe}, -\text{alkyl}, -\text{F}, -\text{Cl}, -\text{NHCOC}_{2}H_{5}, -\text{CF}_{3},\) and \(-\text{benzyl chloride},\) giving the desired product without any decomposition of the starting materials. 2-Naphthyl sulfonamide (\(1na\)) and a Br-substituted substrate, 4-bromo-3-methylbenzenesulfonamide (\(1oa\)), reacted smoothly and produced the desired product in high yield with good selectivity. Higher branch-selectivity was obtained in

### Table 1

| Suitable directing group screening for Rh(II)-catalyzed branched alkylation of aryl sulfonamides with triethylvinylsilane* |
|----------------------------------------------------------|
| **Entry** | **Substrate** | **Yield** | **Branch/Linear** |
| 1 | 3-chloro-2-methylbenzoic acid | n.d. | n.d. |
| 2 | 3-chloro-2-methylbenzoic acid | 0.5 mmol | 5.0 mol% |
| 3 | 2-pyridinylmethylamine | 0.2 mmol | 0.4 mmol |
| 4 | Oxazoline-based aniline | | |
| 5 | 8-aminoquinoline | 49% | 92 : 8 |

* Reaction conditions: sulfonamide (0.2 mmol, 1 equiv.), triethylvinylsilane (0.5 mmol, 2.5 equiv.), [Rh(OAc)_2] (5.0 mol%), and 3-chloro-2-methylbenzoic acid (0.4 mmol) in toluene (0.5 mL) at 160 °C for 24 h. Yields and the ratio of branched and linear isomers were determined by 1H NMR of the crude mixture. N.d. refers to not detected.
the case of para-substituted sulfonamides than the ortho- or meta-substituted substrates, suggesting that steric effects play an important role in controlling the selectivity of the reaction. It should also be noted that no dialkylated products were observed in any of the cases. The use of other vinylsilanes such as trimethylvinylsilane, 1,1,1,3,5,5,5-heptamethyltrisiloxane, dimethylphenylvinylsilane, and diethoxymethylvinylsilane as coupling partners produced the corresponding branch-selective alkylation products in good yields (2ab–ae and 2pa–pc).

To gain insights into the mechanism for this reaction, a series of deuterium labelling experiments were performed (Fig. 2). A significant amount of H/D exchange took place, but only at the ortho-position, when the reaction of sulfonamide 1c with [Rh(OAc)2]2 in the presence of CD3COOD was carried out (Fig. 2a). This result indicates that C–H bond activation is reversible. To collect additional information regarding the mechanism, a reaction between the deuteriated sulfonamide 1c-

### Table 2 Optimization of Rh(II)-catalyzed branched alkylation of aryl sulfonamide 1a with triethylvinylsilane

| Entry | Rh cat. | Additive | 2aa + 3aa | 2aa : 3aa | 4aa |
|-------|---------|----------|-----------|-----------|-----|
| 1     | [Rh(OAc)2]2 | 3-Chloro-2-methyl benzoic acid | 42 | 86 : 14 | 3 |
| 2     | [RhCp*Cl2]2 | 3-Chloro-2-methyl benzoic acid | n.d. | n.d. | n.d. |
| 3     | RhCl(PPh3)3 | 3-Chloro-2-methyl benzoic acid | 8 | 88 : 12 | Trace |
| 4     | [Rh(OAc)cod]2 | 3-Chloro-2-methyl benzoic acid | 27 | 82 : 18 | 4 |
| 5     | [Rh(OAc)2]2 | 2,3-Difluorobenzoic acid | 32 | 85 : 15 | n.d. |
| 6     | [Rh(OAc)2]2 | α-Toluic acid | 48 | 80 : 20 | 5 |
| 7     | [Rh(OAc)2]2 | 3-Chloro-2-methyl benzoic acid | 58 | 75 : 25 | 7 |
| 8     | [Rh(OAc)2]2 | 3-Chloro-2-methyl benzoic acid | 57 | 86 : 14 | 4 |
| 9     | [Rh(OAc)2]2 | 3-Chloro-2-methyl benzoic acid | 70 | 86 : 14 | 2 |
| 10    | [Rh(OAc)2]2 | 3-Chloro-2-methyl benzoic acid | 82 (72) | 86 : 14 | 3 |

* Reaction conditions: sulfonamide (0.2 mmol, 1 equiv.), triethylvinylsilane (0.5 mmol, 2.5 equiv.), [Rh(OAc)2]2 (5.0 mol%), and 3-chloro-2-methylbenzoic acid (0.4 mmol, 2 equiv.) in toluene (0.5 mL) at 160 °C for 24 h. Yields and the ratio of branched and linear isomers were determined by 1H NMR of the crude mixture. Isolated yield is given in parentheses. N.d. refers to not detected. b 5.0 equiv. of triethylvinylsilane. c 6.0 equiv. of triethylvinylsilane.

### Table 3 Substrate scope for branched alkylation of sulfonamides with vinylsilanes

| Entry | Rh cat. | Additive | 2aa + 3aa | 2aa : 3aa | 4aa |
|-------|---------|----------|-----------|-----------|-----|
| 1     | [Rh(OAc)2]2 | 3-Chloro-2-methyl benzoic acid | 42 | 86 : 14 | 3 |
| 2     | [RhCp*Cl2]2 | 3-Chloro-2-methyl benzoic acid | n.d. | n.d. | n.d. |
| 3     | RhCl(PPh3)3 | 3-Chloro-2-methyl benzoic acid | 8 | 88 : 12 | Trace |
| 4     | [Rh(OAc)cod]2 | 3-Chloro-2-methyl benzoic acid | 27 | 82 : 18 | 4 |
| 5     | [Rh(OAc)2]2 | 2,3-Difluorobenzoic acid | 32 | 85 : 15 | n.d. |
| 6     | [Rh(OAc)2]2 | α-Toluic acid | 48 | 80 : 20 | 5 |
| 7     | [Rh(OAc)2]2 | 3-Chloro-2-methyl benzoic acid | 58 | 75 : 25 | 7 |
| 8     | [Rh(OAc)2]2 | 3-Chloro-2-methyl benzoic acid | 57 | 86 : 14 | 4 |
| 9     | [Rh(OAc)2]2 | 3-Chloro-2-methyl benzoic acid | 70 | 86 : 14 | 2 |
| 10    | [Rh(OAc)2]2 | 3-Chloro-2-methyl benzoic acid | 82 (72) | 86 : 14 | 3 |

* Reaction conditions: sulfonamide (0.2 mmol, 1 equiv.), triethylvinylsilane (1.2 mmol, 6 equiv.), [Rh(OAc)2]2 (7.5 mol%), and 3-chloro-2-methylbenzoic acid (0.4 mmol, 2 equiv.) in toluene (0.5 mL) at 160 °C for 24 h. The ratio of branched and linear isomers was determined by 1H NMR of the crude mixture. Yield of alkenylated product 4 is given in parentheses. a 10 mol% catalyst was used. b 10 equiv. of vinylsilane.
and triethylvinylsilane was performed under the optimized reaction conditions, in which 0.34 D atom (2.66 H) was incorporated at the methyl position (β-position), while no D incorporation was detected at the tertiary carbon center (α-position) of product 6 (Fig. 2b). This observation suggests that a hydrometallation mechanism may be involved. The use of CD₃COOD as the only deuterated reagent in a reaction of 1c and triethylvinylsilane gave product 8 in which 0.51 D atom (2.49 H) was incorporated only at the methyl position (β-position) (Fig. 2c). This result implies the involvement of a carbometallation pathway.

The kinetic isotopic effect (KIE) for this reaction was determined in two parallel experiments using an equimolar amount of 1c or deuterated 1c-d₅, and a k_D/k_H ratio of 1.06 was obtained. This observation indicates that the C–H activation step is not the rate limiting step (Fig. 3a). A stoichiometric reaction of 1c and [Rh(OAc)₂]₂ was performed, and it resulted in the formation of a dimeric Rh-complex, 10 (Fig. 3b). To trap any other intermediates, several control experiments were performed in the presence or absence of an acid additive with varying temperature; however, it was not possible to isolate the corresponding rhodacycle. A catalytic reaction of 1c and triethylvinylsilane catalyzed by complex 10 under optimized reaction conditions was performed, and it provides a comparable yield and selectivity of product 2ca (Fig. 3c). This result suggested that complex 10 is involved in the catalytic cycle as an intermediate.

Based on the deuterium studies, we proposed a reaction mechanism that follows two major pathways as shown in Fig. 4. Complexation between Rh(II) and the bidentate sulfonamide initially occurs to form intermediate A, which was isolated as 10 and the structure was confirmed by an X-ray crystallographic analysis (Fig. 3b). Complex A then releases two equivalents of acid to produce B, which is detected in the ¹H NMR spectrum (see the ESI†), followed by a subsequent oxidative addition of the ortho C–H bond of or a Rh-hydride complex, C. The insertion of a vinylsilane into the Rh–H bond in C via a hydrometallation pathway forms intermediate D, which then undergoes reductive elimination to generate E. Finally, the product is released from E in the presence of acid, along with the regeneration of the Rh(II) catalyst. According to this proposed pathway, a D-atom should be incorporated only into the β-position of the product when a deuterated sulfonamide is used. In fact, D-incorporation was observed only at the β-position and no D-incorporation was detected at the α-position (Fig. 2b). However, due to the low D-incorporation we concluded that an alternative mechanism could also be involved, as shown in cycle-Ⅱ. After the formation of C, two molecules of carboxylic acid can be dissociated and covalently

Fig. 2 Deuterium labelling experiments. (a) Reaction of 1c in the presence of CD₃COOD, (b) reaction of 1c-d₅ with triethylvinylsilane, and (c) reaction of 1c with triethylvinylsilane in the presence of CD₃COOD.

Fig. 3 (a) KIE experiment, (b) synthesis of bimetallic Rh-complex 10, and (c) the reaction using complex 10 as a catalyst.
coordinated to the Rh-centre to afford a metallacycle, F. Direct formation of F from B could also be possible. The migratory insertion of an alkene into a Rh–C bond forms G, which could then react with two equivalents of acid to give the product via Rh-complex E. The results of a deuterium labelling experiment using CD$_3$COOD suggest that D-incorporation took place only at the methyl position (β-position) of the product (Fig. 3c), which is consistent with this proposed catalytic cycle-II. We anticipated that the trace amount of alkenylated product had formed via the migratory insertion of an alkene into a Rh–C bond of F followed by β-hydride elimination.

The stabilizing effect of two Rh-centers bonded through a single bond could be useful for facilitating double C–H activation at the same time. The exact reason for this unusual branch selective alkylation is currently under investigation in our laboratory.

**Conclusions**

In summary, we report the first example of Rh(II)-catalyzed branch-selective ortho-C–H alkylation of aryl sulfonamides with vinylsilanes using an 8-aminquinoline auxiliary group. Benzenesulfonamide and para-substituted aryl sulfonamides produced selectively mono-(branched)alkylated products without any double C–H activated byproducts being produced. Based on deuterium labelling experiments, a reasonable catalytic cycle is proposed, in which two parallel catalytic pathways, i.e. hydrometalation and carbometalation pathways, are involved. An investigation of the reaction conditions for achieving other branch-selective C–H alkylation reactions is currently ongoing in our laboratory.

**Conflicts of interest**

There are no conflicts to declare.

**Acknowledgements**

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