Chemical Science

EDGE ARTICLE

View Article Online
View Journal | View Issue

Check for updates

Cite this: *Chem. Sci.*, 2020, **11**, 389

All publication charges for this article have been paid for by the Royal Society of Chemistry

Received 27th August 2019
Accepted 9th November 2019

DOI: 10.1039/c9sc04308j

rsc.li/chemical-science

Rh(II)-catalyzed branch-selective C–H alkylation of aryl sulfonamides with vinylsilanes†

Supriya Rej and Naoto Chatani *

Rhodium(II)-catalyzed unusual branch-selective *ortho*-C–H alkylation of aryl sulfonamides with vinylsilanes was achieved using an 8-aminoquinoline directing group. Notably, the *para*-substituted aryl sulfonamides gave mono-(branched)alkylated products exclusively without the formation of any double C–H alkylated byproducts. The results of deuterium labeling experiments suggest that both hydrometalation and carbometalation pathways are involved in this conversion.

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.[1] In particular, directed C–H alkylation with 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.[2] Following this pioneering reaction, numerous directing groups have been designed for use in regio-selective C–H alkylation reactions.[3] 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 alkenes have been reported (Fig. 1A).[4,5] In this respect, non-directed strategies were discussed for the alkylation of 1,3,4-oxadiazoles (a),[4a] indoles (b and c),[4b,c] benzimidazoles (d, e, and j),[4d,e,h] benzoxazoles (f),[4i] benzothiazoles (g),[4j] pyridines (h),[4f] and azines (i)[4g] 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),[5a] Yoshikai reported a Co-catalyzed branched alkylation of 2-arylpyridine with styrene derivatives (II),[5b] Ramana reported a Ru-catalyzed ketone-directed C3-alkylation of 2-aroylbenzofurans with α,β-unsaturated carbonyl derivatives (III),[5c] Bower reported a carbonyl-directed Ir-catalyzed *ortho*-alkylation of aromatic ketones (IV),[5d] Nishimura reported an Ir-catalyzed alkylation of 2-phenylpyridine derivatives with vinyl ethers (V),[5e] Bower reported an Ir-catalyzed branch-selective *ortho*-alkylation of acetanilides (VI),[5f] and an yttrium-catalyzed *ortho*-alkylation of *N*,*N*-dimethylaniline with alkenes was demonstrated by Hou (VII).[5g] Dong reported an Ir-catalyzed branch selective α-alkylation of ketones with styrenes and unactivated alkenes *via* the use of an enamine directing strategy (VIII).[5h] In 2017, Ackermann reported a Co-catalyzed branch-selective alkylation of indole using unactivated alkenes with a detailed mechanistic explanation (IX).[5i] Yoshikai recently presented a Co-catalyzed N–H imine-directed branch selective alkylation of aromatic imine derivatives with styrenes (X).[5j] 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).[2,6]

Our group recently reported a series of linear selective C–H alkylations of benzamides,[6m,7a–c,g,h] naphthylamides,[8] and sulfonamides[9] with vinyl ketones, acrylate esters, styrenes, *N*-vinylphthalimides, unactivated 1-alkenes, and vinylsilanes using an 8-aminoquinoline or picolinamide directing group, which was first introduced by Daugulis in 2005.[10] Having continuous interest in alkylation reactions,[7–9] 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 sulfonamides[11] with vinylsilanes by taking advantage of an 8-aminoquinoline directing group (Fig. 1C).

Results and discussion

We began our studies by investigating suitable directing groups for the branch-selective alkylation of aryl sulfonamides with triethylvinylsilane in the presence of a $[Rh(OAc)_2]_2$ catalyst.[12]

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565-0871, Japan. E-mail: chatani@chem.eng.osaka-u.ac.jp

† Electronic supplementary information (ESI) available: Experimental details and spectroscopic data. CCDC 1910136, 1918726. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c9sc04308j

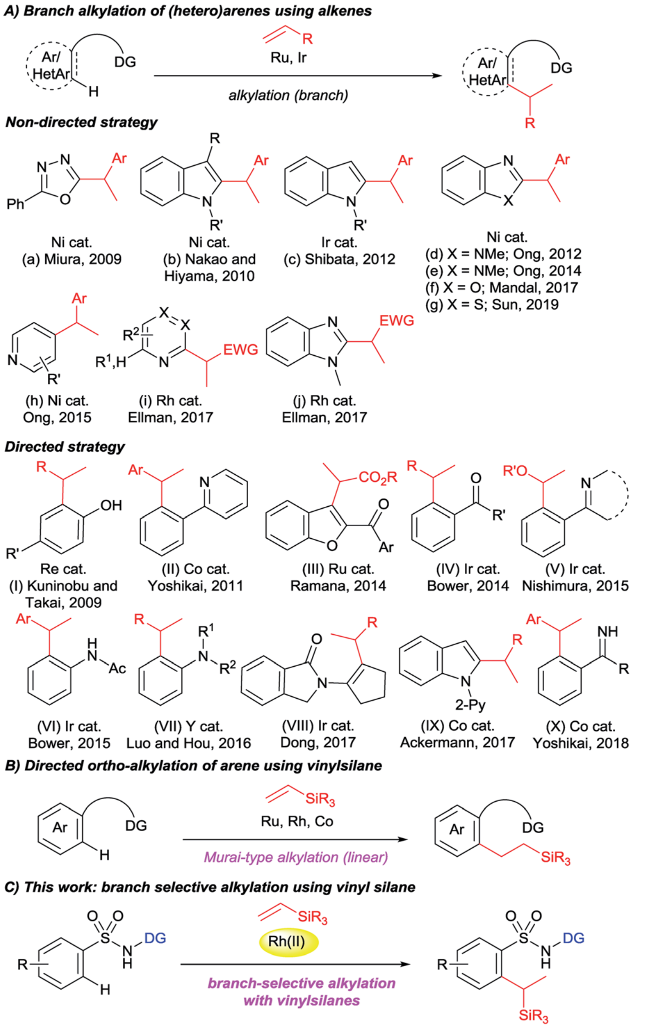
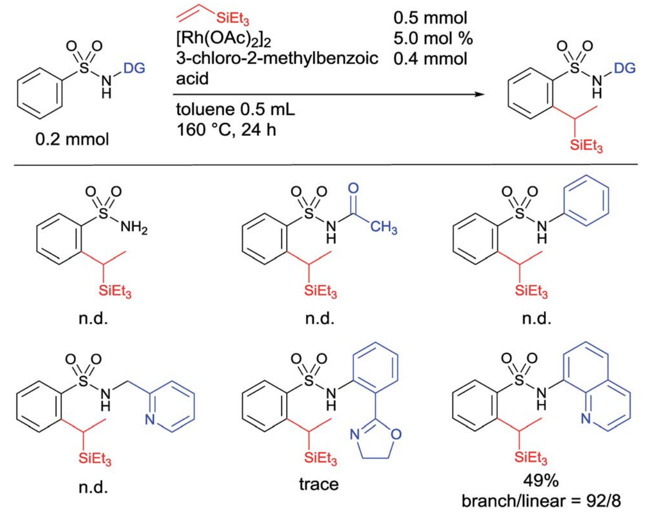


Fig. 1 (A) Literature overview of the branched alkylation of (hetero) arenes with alkenes, (B) directed *ortho*-alkylation of arenes with vinylsilanes, and (C) this work: Rh(II)-catalyzed branched alkylation of sulfonamides with vinylsilanes.

Table 1 Suitable directing group screening for Rh(II)-catalyzed branched alkylation of aryl sulfonamides with triethylvinylsilane[a]



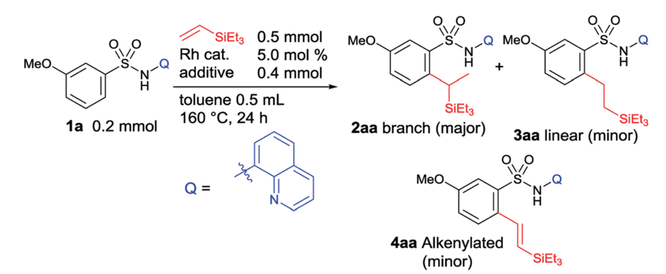
[a] Reaction conditions: sulfonamide (0.2 mmol, 1 equiv.), triethylvinylsilane (0.5 mmol, 2.5 equiv.), $[Rh(OAc)_2]_2$ (5.0 mol%), and 3-chloro-2-methylbenzoic acid (0.4 mmol) in toluene (0.5 mL) at 160 °C for 24 h. Yields and the ratio of branched and linear isomers were determined by ^{1}H NMR of the crude mixture. N.d. refers to not detected.

The reaction of benzenesulfonamide with triethylvinylsilane in the presence of $[Rh(OAc)_2]_2$ 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(II) 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 –OMe, –alkyl, –F, –Cl, –$NHCOCH_3$, –CF_3, and –benzylic 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

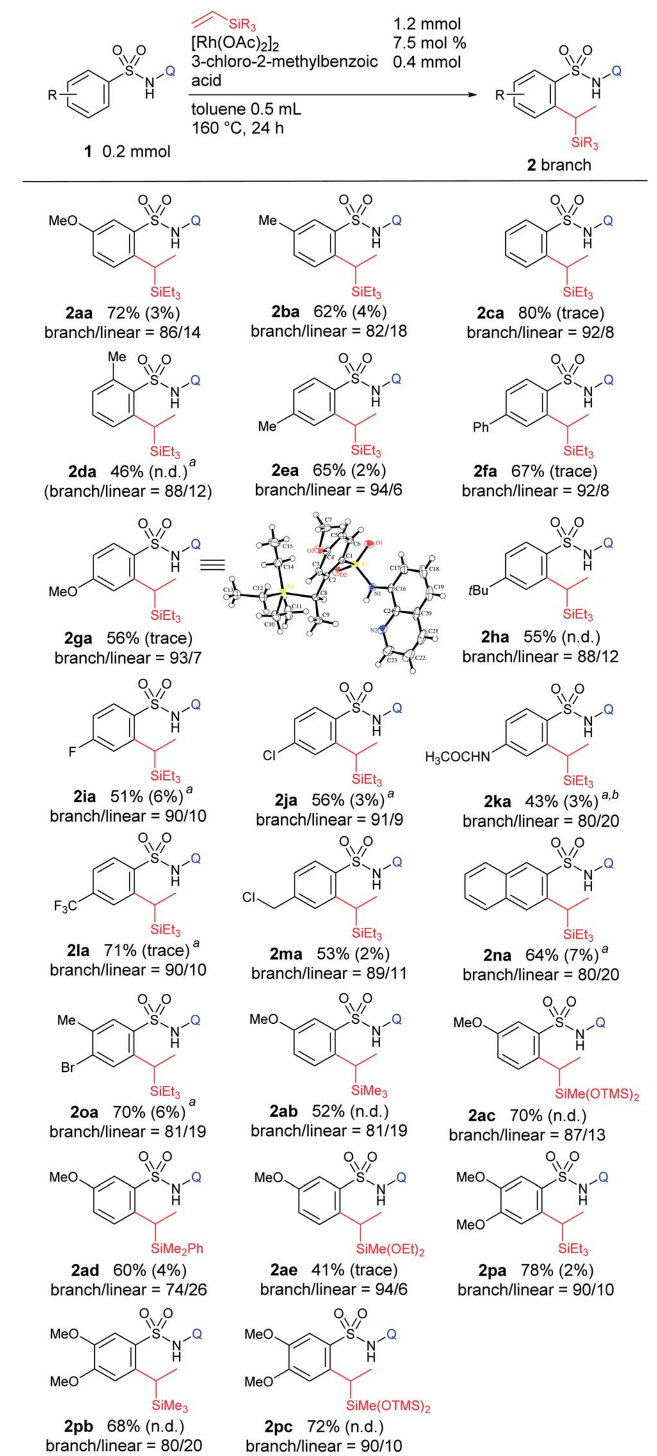
Table 2 Optimization of Rh(II)-catalyzed branched alkylation of aryl sulfonamide **1a** with triethylvinylsilane[a]



Entry	Rh cat.	Additive	2aa + 3aa	2aa : 3aa	4aa
1	$[Rh(OAc)_2]_2$ (5.0 mol%)	3-Chloro-2-methyl benzoic acid	42	86 : 14	3
2	$[RhCp^*Cl_2]_2$ (5.0 mol%)	3-Chloro-2-methyl benzoic acid	n.d.	n.d.	n.d.
3	$RhCl(PPh_3)_3$ (10.0 mol%)	3-Chloro-2-methyl benzoic acid	8	88 : 12	Trace
4	$[Rh(OAc)cod]_2$ (5.0 mol%)	3-Chloro-2-methyl benzoic acid	27	82 : 18	4
5	$[Rh(OAc)_2]_2$ (5.0 mol%)	2,3-Difluorobenzoic acid	32	85 : 15	n.d.
6	$[Rh(OAc)_2]_2$ (5.0 mol%)	*o*-Toluic acid	48	80 : 20	5
7	$[Rh(OAc)_2]_2$ (5.0 mol%)	Pivalic acid	58	75 : 25	5
8[b]	$[Rh(OAc)_2]_2$ (5.0 mol%)	3-Chloro-2-methyl benzoic acid	57	86 : 14	4
9[b]	$[Rh(OAc)_2]_2$ (7.5 mol%)	3-Chloro-2-methyl benzoic acid	70	86 : 14	2
10[c]	$[Rh(OAc)_2]_2$ (7.5 mol%)	3-Chloro-2-methyl benzoic acid	82 (72)	86 : 14	3

[a] 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[a]



2aa 72% (3%) branch/linear = 86/14
2ba 62% (4%) branch/linear = 82/18
2ca 80% (trace) branch/linear = 92/8
2da 46% (n.d.)[a] (branch/linear = 88/12)
2ea 65% (2%) branch/linear = 94/6
2fa 67% (trace) branch/linear = 92/8
2ga 56% (trace) branch/linear = 93/7
2ha 55% (n.d.) branch/linear = 88/12
2ia 51% (6%)[a] branch/linear = 90/10
2ja 56% (3%)[a] branch/linear = 91/9
2ka 43% (3%)[a,b] branch/linear = 80/20
2la 71% (trace)[a] branch/linear = 90/10
2ma 53% (2%) branch/linear = 89/11
2na 64% (7%)[a] branch/linear = 80/20
2oa 70% (6%)[a] branch/linear = 81/19
2ab 52% (n.d.) branch/linear = 81/19
2ac 70% (n.d.) branch/linear = 87/13
2ad 60% (4%) branch/linear = 74/26
2ae 41% (trace) branch/linear = 94/6
2pa 78% (2%) branch/linear = 90/10
2pb 68% (n.d.) branch/linear = 80/20
2pc 72% (n.d.) branch/linear = 90/10

[a] 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. [b] 10 mol% catalyst was used. [c] 10 equiv. of vinylsilane.

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 CD_3COOD 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 deuterated sulfonamide **1c**-

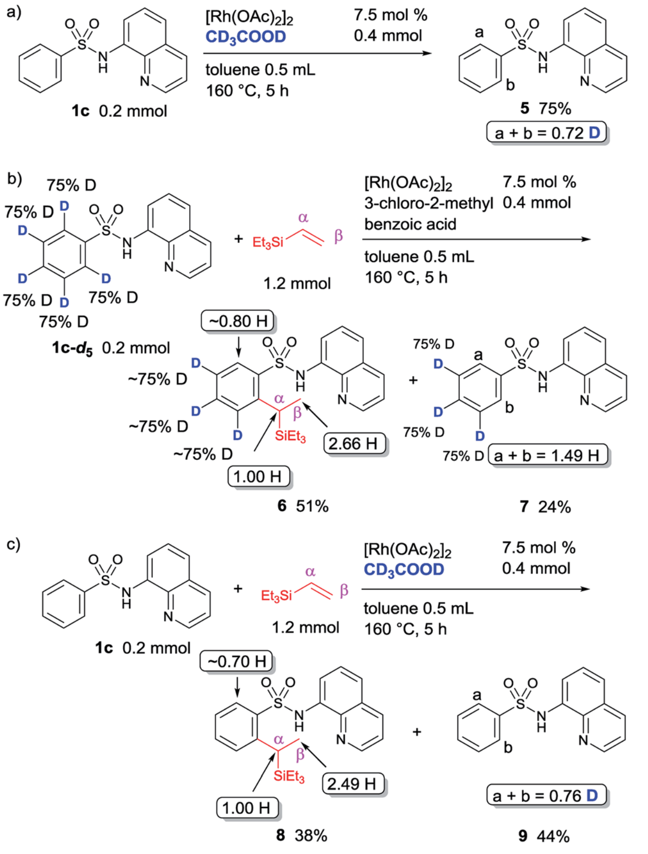


Fig. 2 Deuterium labelling experiments. (a) Reaction of **1c** in the presence of CD_3COOD, (b) reaction of **1c-*d*₅** with triethylvinylsilane, and (c) reaction of **1c** with triethylvinylsilane in the presence of CD_3COOD.

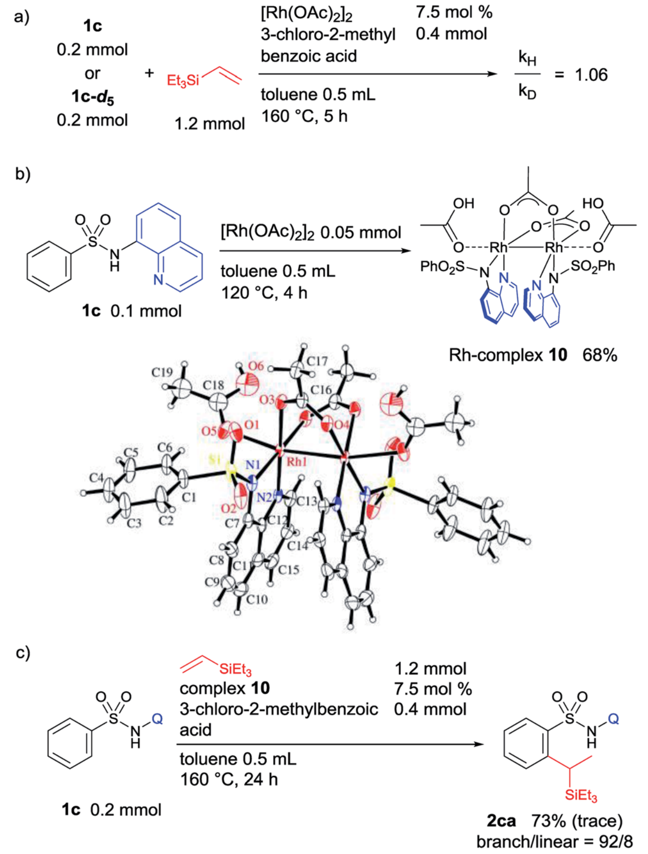


Fig. 3 (a) KIE experiment, (b) synthesis of bimetallic Rh-complex **10**, and (c) the reaction using complex **10** as a catalyst.

***d*$_5$** 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 CD_3COOD 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-*d*$_5$**, and a k_H/k_D 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 ^{1}H NMR spectrum (see the ESI†),[13] followed by a subsequent oxidative addition of the *ortho* C–H bond to form a Rh-hydride complex, **C**. The insertion of a vinylsilane into the Rh–H bond in **C** *via* a hydrometalation pathway forms intermediate **D**,[14] 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

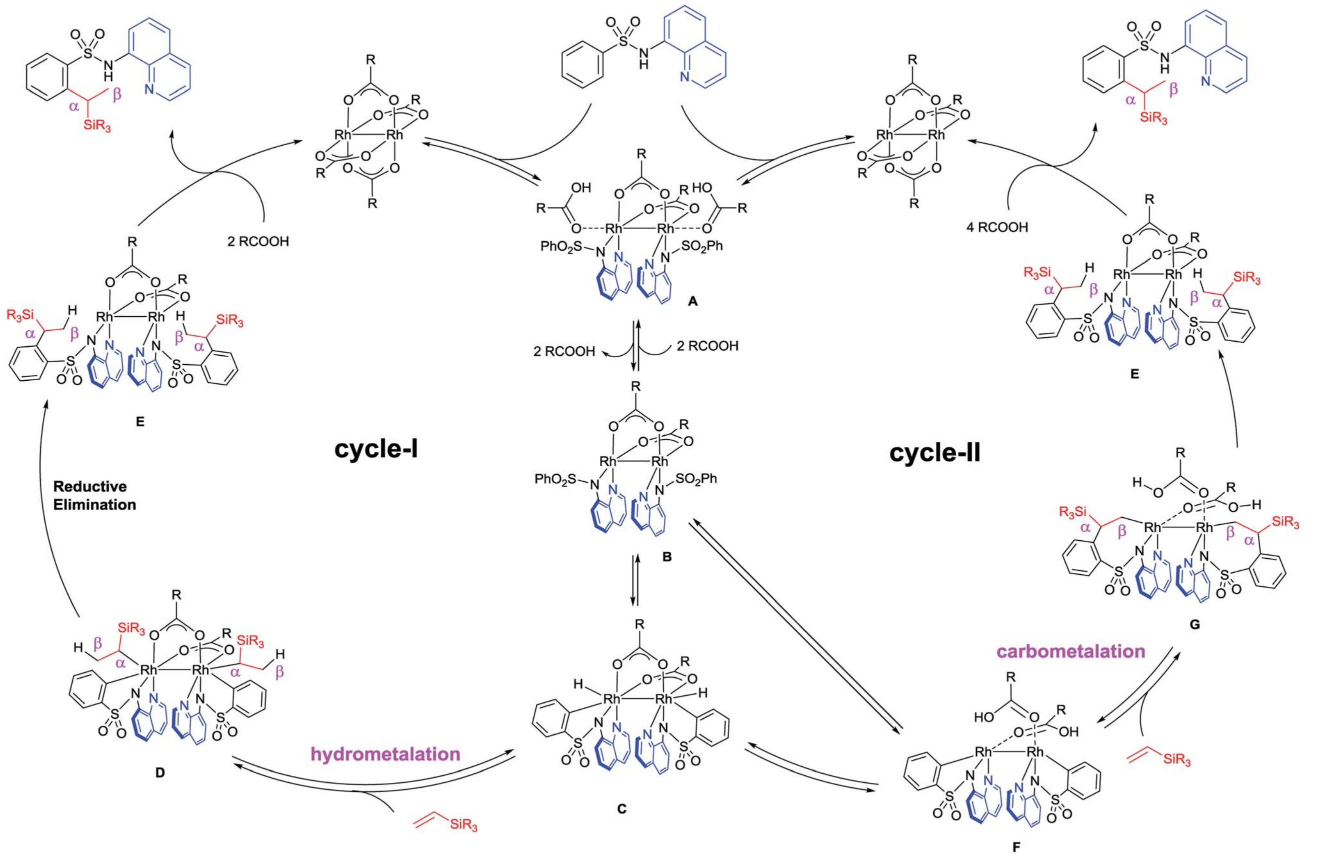


Fig. 4 Plausible mechanistic pathways.

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**,[15] 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_3COOD 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.[16] 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.[17]

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-aminoquinoline 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

This work was supported by a Grant in Aid for Specially Promoted Research by MEXT (17H06091).

Notes and references

1 For selected recent reviews on directing group assisted C–H functionalization, see: (*a*) Z. Chen, B. Wang, J. Zhang, W. Yu, Z. Liu and Y. Zhang, *Org. Chem. Front.*, 2015, **2**, 1107–1295; (*b*) Z. Huang, H. N. Lim, F. Mo, M. C. Young and G. Dong, *Chem. Soc. Rev.*, 2015, **44**, 7764–7786; (*c*) T. Gensch, M. N. Hopkinson, F. Glorius and J. Wencel-Delord, *Chem. Soc. Rev.*, 2016, **45**, 2900–2936; (*d*) J. He, M. Wasa, K. S. L. Chan, Q. Shao and J.-Q. Yu, *Chem. Rev.*, 2017, **117**, 8754–8786; (*e*) Y. Yang, J. Lan and J. You, *Chem. Rev.*, 2017,

117, 8787–8863; (*f*) Y. Park, Y. Kim and S. Chang, *Chem. Rev.*, 2017, **117**, 9247–9301; (*g*) J. R. Hummel, J. A. Boerth and J. A. Ellman, *Chem. Rev.*, 2017, **117**, 9163–9227; (*h*) C. Sambiagio, D. Schönbauer, R. Blieck, T. Dao-Huy, G. Pototschnig, P. Schaaf, T. Wiesinger, M. F. Zia, J. Wencel-Delord, T. Besset, B. U. W. Maes and M. Schnürch, *Chem. Soc. Rev.*, 2018, **47**, 6603–6743; (*i*) J. C. K. Chu and T. Rovis, *Angew. Chem., Int. Ed.*, 2018, **57**, 62–101; (*j*) S. Rej and N. Chatani, *Angew. Chem., Int. Ed.*, 2019, **58**, 8304–8329; (*k*) A. Dey, S. K. Sinha, T. K. Achar and D. Maiti, *Angew. Chem., Int. Ed.*, 2019, **58**, 10820–10843; (*l*) P. Gandeepan, T. Müller, D. Zell, G. Cera, S. Warratz and L. Ackermann, *Chem. Rev.*, 2019, **119**, 2192–2452; (*m*) P. Gandeepan, N. Kaplaneris, S. Santoro, L. Vaccaro and L. Ackermann, *ACS Sustainable Chem. Eng.*, 2019, **7**, 8023–8040; (*n*) S. M. Khake and N. Chatani, *Trends in Chemistry*, 2019, **1**, 524–539.

2 S. Murai, F. Kakiuchi, S. Sekine, Y. Tanaka, A. Kamatani, M. Sonoda and N. Chatani, *Nature*, 1993, **366**, 529–531.

3 For reviews on directing group assisted C–H alkylation reaction, see: (*a*) G. E. M. Crisenza and J. F. Bower, *Chem. Lett.*, 2016, **45**, 2–9; (*b*) Z. Dong, Z. Ren, S. J. Thompson, Y. Xu and G. Dong, *Chem. Rev.*, 2017, **117**, 9333–9403; (*c*) N. Chatani, *Bull. Chem. Soc. Jpn.*, 2018, **91**, 211–222; (*d*) G. Evano and C. Theunissen, *Angew. Chem., Int. Ed.*, 2019, **58**, 7202–7236.

4 For papers on non-directed branch-selective alkylation, see: (*a*) T. Mukai, K. Hirano, T. Satoh and M. Miura, *J. Org. Chem.*, 2009, **74**, 6410–6413; (*b*) Y. Nakao, N. Kashihara, K. S. Kanyiva and T. Hiyama, *Angew. Chem., Int. Ed.*, 2010, **49**, 4451–4454; (*c*) S. Pan, N. Ryu and T. Shibata, *J. Am. Chem. Soc.*, 2012, **134**, 17474–17477; (*d*) W.-C. Shih, W.-C. Chen, Y.-C. Lai, M.-S. Yu, J.-J. Ho, G.-P. A. Yap and T.-G. Ong, *Org. Lett.*, 2012, **14**, 2046–2049; (*e*) W.-C. Chen, Y.-C. Lai, W.-C. Shih, M.-S. Yu, G. P. A. Yap and T.-G. Ong, *Chem.–Eur. J.*, 2014, **20**, 8099–8105; (*f*) W.-C. Lee, C.-H. Chen, C.-Y. Liu, M.-S. Yu, Y.-H. Lin and T.-G. Ong, *Chem. Commun.*, 2015, **51**, 17104–17107; (*g*) G. Tran, K. D. Hesp, V. Mascitti and J. A. Ellman, *Angew. Chem., Int. Ed.*, 2017, **56**, 5899–5903; (*h*) G. Tran, D. Confair, K. D. Hesp, V. Mascitti and J. A. Ellman, *J. Org. Chem.*, 2017, **82**, 9243–9252; (*i*) G. Vijaykumar, A. Jose, P. K. Vardhanapu, P. Sreejyothi and S. K. Mandal, *Organometallics*, 2017, **36**, 4753–4758; (*j*) R.-P. Li, Z.-W. Shen, Q.-J. Wu, J. Zhang and H.-M. Sun, *Org. Lett.*, 2019, **21**, 5055–5058.

5 For papers on directing group assisted branch-selective alkylation, see: (*a*) Y. Kuninobu, T. Matsuki and K. Takai, *J. Am. Chem. Soc.*, 2009, **131**, 9914–9915; (*b*) K. Gao and N. Yoshikai, *J. Am. Chem. Soc.*, 2011, **133**, 400–402; (*c*) Y. Kommagalla, K. Srinivas and C. V. Ramana, *Chem.–Eur. J.*, 2014, **20**, 7884–7889; (*d*) G. E. M. Crisenza, N. G. McCreanor and J. F. Bower, *J. Am. Chem. Soc.*, 2014, **136**, 10258–10261; (*e*) Y. Ebe and T. Nishimura, *J. Am. Chem. Soc.*, 2015, **137**, 5899–5902; (*f*) G. E. M. Crisenza, O. O. Sokolova and J. F. Bower, *Angew. Chem., Int. Ed.*, 2015, **54**, 14866–14870; (*g*) G. Song, G. Luo, J. Oyamada, Y. Luo and Z. Hou, *Chem. Sci.*, 2016, **7**, 5265–5270; (*h*) D. Xing and G. Dong, *J. Am. Chem. Soc.*, 2017, **139**, 13664–13667; (*i*) D. Zell, M. Bursch, V. Müller, S. Grimme and L. Ackermann, *Angew. Chem., Int. Ed.*, 2017, **56**, 10378–10382; (*j*) W. Xu and N. Yoshikai, *Org. Lett.*, 2018, **20**, 1392–1395.

6 For papers on directing group assisted linear C–H alkylation using vinylsilanes, see: (*a*) F. Kakiuchi, T. Sato, M. Yamauchi, N. Chatani and S. Murai, *Chem. Lett.*, 1999, **28**, 19–20; (*b*) F. Kakiuchi, M. Sonoda, T. Tsujimoto, N. Chatani and S. Murai, *Chem. Lett.*, 1999, **28**, 1083–1084; (*c*) F. Kakiuchi, T. Sato, K. Igi, N. Chatani and S. Murai, *Chem. Lett.*, 2001, **30**, 386–387; (*d*) F. Kakiuchi, H. Ohtaki, M. Sonoda, N. Chatani and S. Murai, *Chem. Lett.*, 2001, **30**, 918–919; (*e*) F. Kakiuchi, T. Tsujimoto, M. Sonoda, N. Chatani and S. Murai, *Synlett*, 2002, 948–951; (*f*) R. Martinez, M. O. Simon, R. Chevalier, C. Pautigny, J.-P. Genet and S. Darses, *J. Am. Chem. Soc.*, 2009, **131**, 7887–7895; (*g*) M.-O. Simon, J.-P. Genet and S. Darses, *Org. Lett.*, 2010, **12**, 3038–3041; (*h*) M.-O. Simon, R. Martinez, J.-P. Genet and S. Darses, *J. Org. Chem.*, 2010, **75**, 208–210; (*i*) K. Gao and N. Yoshikai, *Angew. Chem., Int. Ed.*, 2011, **50**, 6888–6892; (*j*) Z. Ding and N. Yoshikai, *Beilstein J. Org. Chem.*, 2012, **8**, 1536–1542; (*k*) M. Schinkel, L. Wang, K. Bielefeld and L. Ackermann, *Org. Lett.*, 2014, **16**, 1876–1879; (*l*) W. Xu and N. Yoshikai, *Angew. Chem., Int. Ed.*, 2016, **55**, 12731–12735; (*m*) C. Wang, S. Rej and N. Chatani, *Chem. Lett.*, 2019, **48**, 1185–1187.

7 For Ru- or Rh-catalyzed 8-aminoquinoline directed C–H alkylation by our group, see: (*a*) G. Rouquet and N. Chatani, *Chem. Sci.*, 2013, **4**, 2201–2208; (*b*) K. Shibata and N. Chatani, *Org. Lett.*, 2014, **16**, 5148–5151; (*c*) K. Shibata, T. Yamaguchi and N. Chatani, *Org. Lett.*, 2015, **17**, 3584–3587; (*d*) K. Shibata and N. Chatani, *Chem. Sci.*, 2016, **7**, 240–245; (*e*) K. Shibata, S. Natsui, M. Tobisu, Y. Fukumoto and N. Chatani, *Nat. Commun.*, 2017, **8**, 1448; (*f*) Q. He, T. Yamaguchi and N. Chatani, *Org. Lett.*, 2017, **19**, 4544–4547; (*g*) Q. He and N. Chatani, *J. Org. Chem.*, 2018, **83**, 13587–13594; (*h*) T. Yamaguchi, S. Natsui, K. Shibata, K. Yamazaki, S. Rej, Y. Ano and N. Chatani, *Chem.–Eur. J.*, 2019, **25**, 6915–6919.

8 For a paper on picolinamide directed C(8)–H alkylation of 1-naphthylamine derivatives, see: S. Rej and N. Chatani, *ACS Catal.*, 2018, **8**, 6699–6706.

9 For a paper on 8-aminoquinoline directed C–H alkylation of sulfonamides, see: S. Rej and N. Chatani, *Chem. Commun.*, 2019, **55**, 10503–10506.

10 V. G. Zaitsev, D. Shabashov and O. Daugulis, *J. Am. Chem. Soc.*, 2005, **127**, 13154–13155.

11 For the importance of sulfonamides, see: (*a*) J. D. Larsen and H. Bundgaard, *Int. J. Pharm.*, 1987, **37**, 87–95; (*b*) J. Drews, *Science*, 2000, **287**, 1960–1964; (*c*) A. Scozzafava, T. Owa, A. Mastrolorenzo and C. T. Supuran, *Curr. Med. Chem.*, 2003, **10**, 925–953.

12 Besides carbene and nitrene transfer reactions, the use of a Rh(II) catalyst in C–H alkylation reactions is very rare in the literature. For a C–H arylation, see: J. Kwak, M. Kim

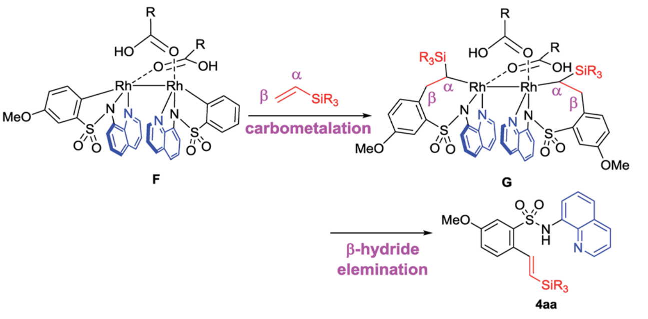
and S. Chang, Rh(NHC)-catalyzed direct and selective arylation of quinolines at the 8-position, *J. Am. Chem. Soc.*, 2011, **133**, 3780–3783.

13 Complex **11**, which is similar to **B**, was detected by ^{1}H NMR when complex **10** was washed with hexane and then dried under vacuum (ESI†). This complex was also detected when the reaction of sulfonamide **1c** and $[Rh(OAc)_2]_2$ was carried out in the presence of 3-chloro-2-methylbenzoic acid.

14 For a paper on metal–hydride insertion into alkenes, see: J. Yu and J. B. Spencer, *J. Am. Chem. Soc.*, 1997, **119**, 5257–5258.

15 For papers on the migratory insertion of metal–C bonds into alkenes, see: (*a*) J. Ledford, C. S. Shultz, D. P. Gates, P. S. White, J. M. DeSimone and M. Brookhart, *Organometallics*, 2001, **20**, 5266–5276; (*b*) C. N. Iverson and W. D. Jones, *Organometallics*, 2001, **20**, 5745–5750; (*c*) A. Haynes, C. E. Haslam, K. J. Bonnington, L. Parish, H. Adams, S. E. Spey, T. B. Marder and D. N. Coventry, *Organometallics*, 2004, **23**, 5907–5909; (*d*) J. Vicente, J.-A. Abad, W. Förtsch, M.-J. López-Sáez and P. G. Jones, *Organometallics*, 2004, **23**, 4414–4429; (*e*) L. Li, Y. Jiao, W. W. Brennessel and W. D. Jones, *Organometallics*, 2010, **29**, 4593–4605; (*f*) Y. Jiao, M. E. Evans, J. Morris, W. W. Brennessel and W. D. Jones, *J. Am. Chem. Soc.*, 2013, **135**, 6994–7004.

16 Alkenylated products such as **4aa** were obtained from β-hydride elimination in complex **G**, which is responsible for the formation of a linear alkylated product.



17 The intermediacy of mono-nuclear Rh species cannot be excluded.