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Rhodium catalyzed template-assisted distal *para*-C–H olefination†

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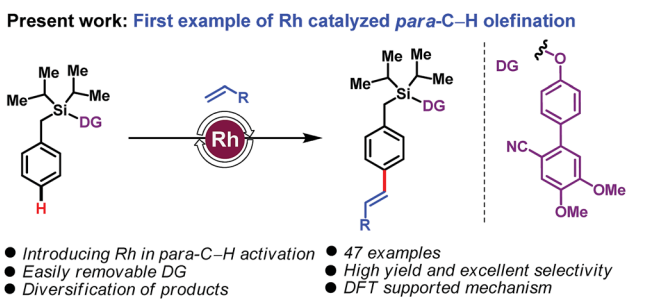
Rhodium catalysis has been extensively used for *ortho*-C–H functionalization reactions, and successfully extended to *meta*-C–H functionalization. Its application to *para*-C–H activation remains an unmet challenge. Herein we disclose the first example of such a reaction, with the Rh-catalyzed *para*-C–H olefination of arenes. The use of a Si-linked cyanobiphenyl unit as a traceless directing group leads to highly *para*-selective arene–olefin couplings.

The transformation of carbon–hydrogen (C–H) bonds into diverse classes of carbon–carbon (C–C) and carbon–heteroatom (C–X) bonds is a cornerstone of organic synthesis. There is intense interest in the discovery of new strategies for regioselective C–H functionalization.[1] A daunting challenge is imposed by the innate inertness of C–H bonds combined with the subtle reactivity differences among the C–H bonds of a given substrate. Directing group (DG)-assisted transition metal-catalyzed C–H activation has proven a successful strategy for regioselective C–H functionalizations in a general and predictable manner.[2] Most commonly coordination of a directing group to a transition metal to form a kinetically and thermodynamically stable 5- or 6-membered metallacycle is used to achieve *ortho*-C–H functionalization. In sharp contrast, distal C–H activation of *meta*[3] and *para*[4] sites is more challenging. In particular, *para*-C–H activation, which entails the formation of large macrocyclophane type metallacyclic intermediates, has remained elusive.[5] In a recent breakthrough, palladium-catalyzed systems employing a carefully designed 'D-shaped' directing group/linker template, based on a cyanobiphenyl motif, led to the first examples of distal *para*-C–H olefinations and acetoxylations.[5,6] Subsequent modifications of the 1st generation DGs through steric and electronic tuning led to 2nd generation DGs capable of effecting *para*-selective silylations[7] and acylations.[8]

To the best of our knowledge, for template assisted *para*-selective functionalization palladium catalysis has been employed so far; albeit, other transition metals are also known to deliver *para*-selective functionalization relying on steric and electronic governance.[5–9] As part of our ongoing interest in C–H functionalization, we have now translated this reaction into the realm of rhodium catalysis and we report here the first example of a Rh-catalyzed *para*-C–H olefination. Existing Rh-catalyzed approaches to C–H activation,[10] using Rh(I)/Rh(III) redox cycles, are complementary to the Pd(0)/Pd(II) or Pd(II)/Pd(IV) cycles prevalent in palladium catalysis. The use of Rh offers benefits over Pd: (a) in contrast to Pd catalysis, which usually requires super-stoichiometric quantities of silver salts, Rh catalysis can be performed with alternative, often cheaper, oxidants; (b) compared with Pd catalysis, which employ monoprotected amino acids (MPAA) as ligands, the different coordination environment of Rh is expected to provide advantageous opportunities for stereoselective synthesis; and (c) importantly, Rh-catalysis does not require use of hexafluoroisopropanol (HFIP), often unavoidable in Pd-catalysed distal C–H activation. With these thoughts in mind, we set about examining a Rh-catalyzed, DG-assisted distal *para*-C–H olefination, as shown in Scheme 1.

We commenced with the olefination of toluene scaffold $\mathbf{DG_1}$ by ethyl acrylate (Scheme 2). Our first attempt, using



Scheme 1 Rh-catalyzed *para*-C–H olefination.

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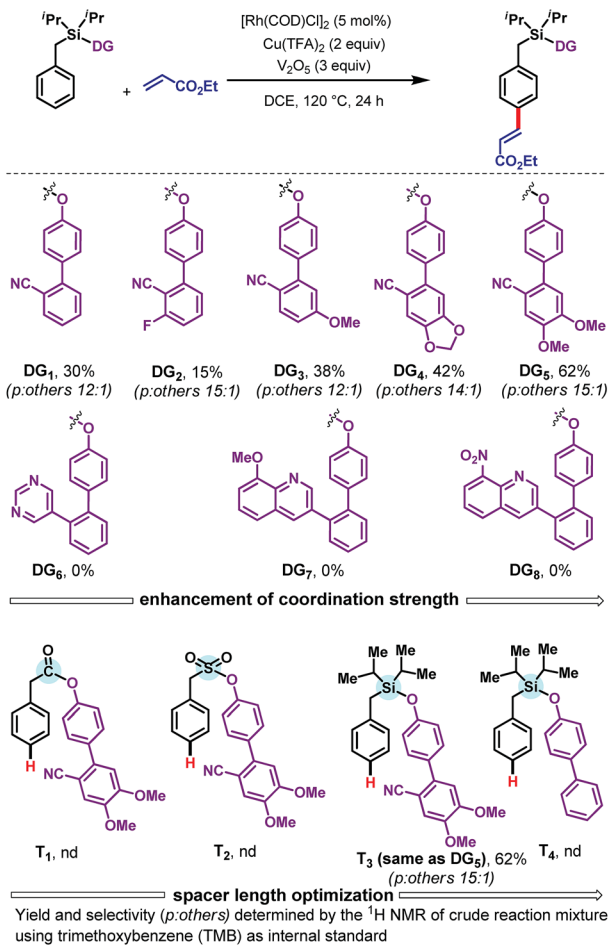
$[Rh(COD)Cl]_2$ (5 mol%) as catalyst, *N*-Ac-Gly-OH (10 mol%) as ligand, and AgOAc (3 equiv.) as oxidant, was unsuccessful. However, use of copper trifluoroacetate $[Cu(TFA)_2]$ as oxidant with V_2O_5 as a co-oxidant provided the desired *para*-olefinated product in 30% yield. Encouraged by this initial result, we examined how the outcome could be improved by modifying the DG (Scheme 2). Analysis of cyano-based DGs ($\mathbf{DG_1}$–$\mathbf{DG_5}$) showed that the presence of an electron-withdrawing fluorine substituent ($\mathbf{DG_2}$) diminished the yield to 15% whereas an electron donating methoxy group ($\mathbf{DG_3}$) elevated the yield to 38%. By further enhancing the electron richness of the DG, the piperonal derivative $\mathbf{DG_4}$ afforded a 42% yield of the olefinated product. The dimethoxy-substituted $\mathbf{DG_5}$ gave a further improvement in yield, to 62%, with 15 : 1 *para* selectivity. The strong σ-donating DGs $\mathbf{DG_6}$–$\mathbf{DG_8}$ failed to provide any of the desired olefinated products. A range of different tethers, containing carbonyl ($\mathbf{T_1}$), sulfonyl ($\mathbf{T_2}$), and silyl ($\mathbf{T_3}$) linkers, were tested, as was a nitrile-free biphenyl template ($\mathbf{T_4}$); only the silyl based template $\mathbf{T_3}$ successfully delivered the desired olefinated product under the Rh-catalyzed conditions. These results indicate that the combination of sterically bulky silyl linker, nitrile group, and alkoxy groups present in $\mathbf{DG_5}$ is crucial for obtaining good yields of the *para*-olefinated product.



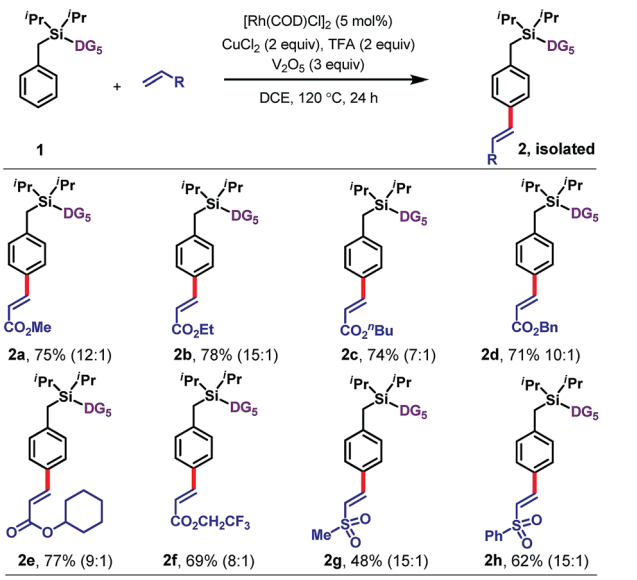
Scheme 2 Evaluation of directing groups.[11]

Using best-performing directing group $\mathbf{DG_5}$, we optimized the reaction with respect to oxidants. A wide variety of silver and copper salts were tested.[11] In contrast to Pd-catalyzed olefinations, silver salts were found to be ineffectual in these Rh-catalyzed reactions, delivering the olefinated products in only trace amounts. Use of $Cu(TFA)_2$ as the oxidant in conjunction with V_2O_5 as a co-oxidant gave a 62% yield of olefinated product with excellent (15 : 1) *para* selectivity. Use of $CuCl_2$ provided a lower (30%) yield of product, but a combination of $CuCl_2$, V_2O_5 and trifluoroacetic acid (TFA) furnished the olefinated product in excellent (85%) yield, with 15 : 1 *para* selectivity.[11] Interestingly, in the absence of either V_2O_5 or TFA, the yield was significantly lower (40% and 30%, respectively). Other acidic additives such as acetic acid (AcOH), triflic acid (CF_3SO_3H) and pivalic acid (Piv–OH) failed to yield the *para*-olefinated product.[11]

With optimized conditions in hand, we explored the scope of the reaction with respect to olefin (Table 1), arene (Tables 2 and 3), and benzylic substituents (Table 4). With respect to the olefin coupling partner (Table 1), a range of acrylates reacted efficiently, including alkyl acrylates **2a**–**2d**, cyclohexyl acrylate **2e**, and trifluoroethyl acrylate **2f**. The olefinated products were obtained in excellent yields with synthetically useful *para*-selectivities ranging from 7 : 1 to 15 : 1. Apart from acrylates, vinyl sulfones including methyl vinyl sulfone (**2g**) and phenyl vinyl sulfone (**2h**) also gave the olefinated products, in 48% and 62% yields, respectively.

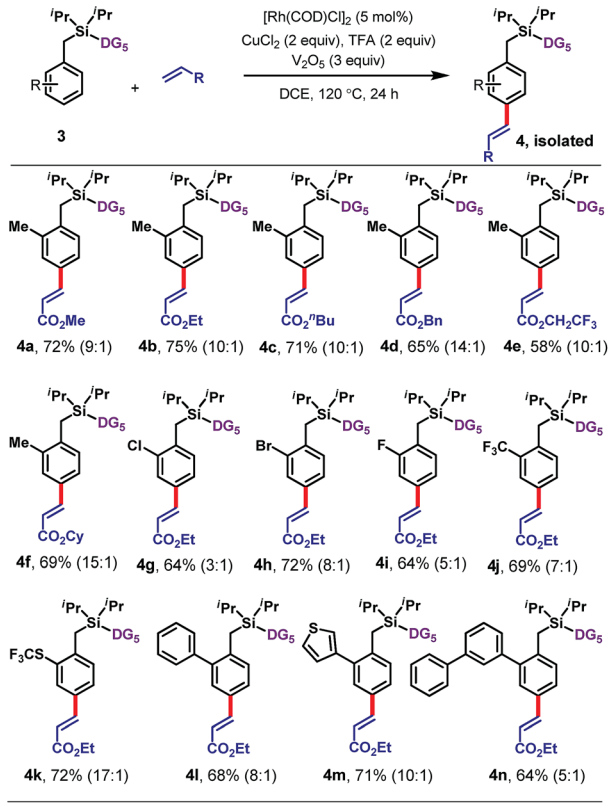
Next an array of substituted arenes was examined (Tables 2 and 3). For monosubstituted arenes, excellent yields and selectivities were obtained irrespective of the electronic nature of the substituent (Table 2). Both electron-rich and electron-deficient arenes were well tolerated, providing yields of up to 75% with upto 17 : 1 *para* selectivity.

Table 1 Scope of olefin coupling partners[a11]



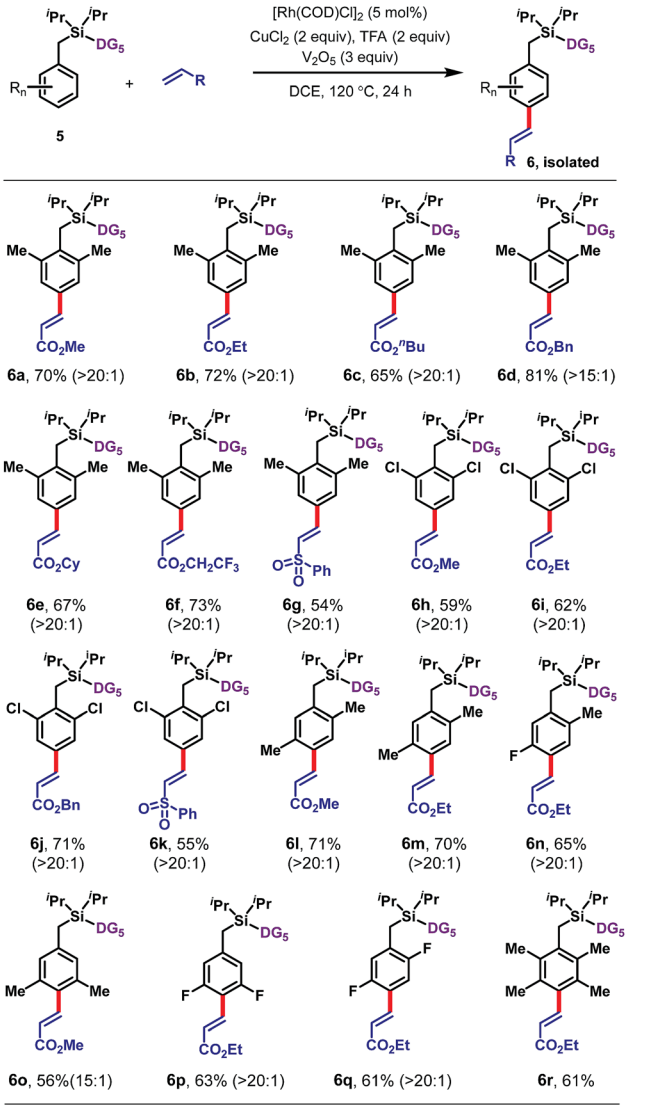
[a] Ratio of *para*: others determined by the ^1H NMR of crude reaction mixture.

Table 2 Scope of monosubstituted toluene derivatives[a11]



[a] Ratio of *para*: others determined by the ^{1}H NMR of crude reaction mixture.

Table 3 Scope of disubstituted toluene derivatives in Rh-catalyzed *para*-C–H olefination[a11]



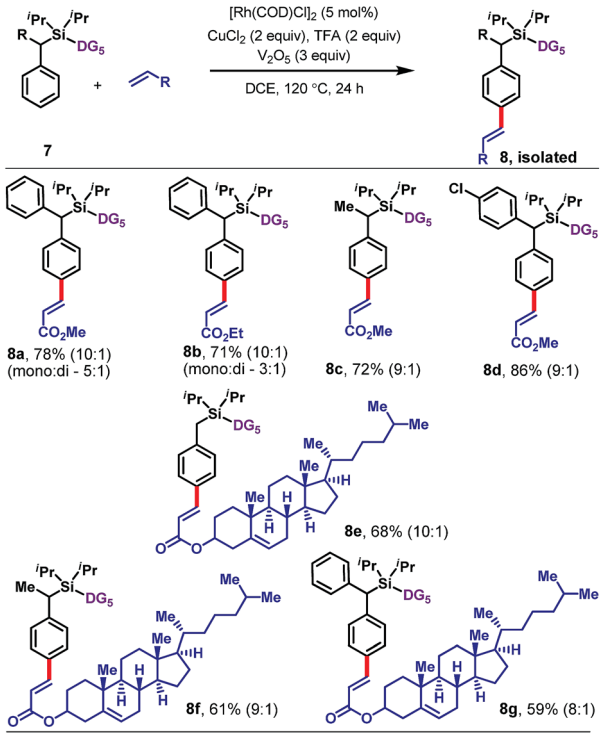
[a] Ratio of *para*: others determined by the ^{1}H NMR of crude reaction mixture.

Disubstituted arenes were also extremely well tolerated (Table 3). The reaction was successfully applied to a range of 2,2, 2,5, 3,5 and 2,6-disubstituted toluenes containing methyl, fluoro, and/or chloro substituents (**6a–6q**). The selectivities of these reactions were generally higher than those observed for monosubstituted arenes, with all ≥15 : 1 *para* selective. Even a tetramethyl-substituted arene was tolerated, reacting with ethyl acrylate to give **6r** in 61% yield.

The protocol is also applicable to α-substituted toluene derivatives (Table 4). Substrates bearing methyl, phenyl, or substituted phenyl substituents at the benzylic position reacted with methyl or ethyl acrylate to afford *para*-olefinated products **8a–8d**. The reaction also worked well with a more complex olefin coupling partner, namely, the acrylate derived from cholesterol, which furnished **8e–8g** in 59–68% yield.

The **DG$_5$** directing group can be readily removed from the olefinated product in several ways (Scheme 3). Treatment of **2b** with TBAF furnished the desilylated product **9** in 92% yield and allowed the **DG$_5$** alcohol **10** to be recovered in 88% yield for reutilization. Alternatively, treatment of **2b** with *p*-TSA generated the corresponding silanol derivative **11** in 82% yield along with an 85% recovery of the **DG$_5$** alcohol. In principle, silanol **11** could be further used as a directing group for *ortho* functionalization. Therefore, the silyl-linked **DG$_5$** represents a traceless directing group enabling access to multi-functionalized arenes. While the *para*-olefinated product **6g** has been treated with KF, $KHCO_3$ and H_2O_2, it produced the corresponding silanol (**12**). The silanol derivative was then employed under modified Tamao's oxidation condition to produce corresponding benzyl alcohol (**13**). Another derivative **2c** was treated under similar condition to provide the benzyl alcohol which subsequently oxidized to the corresponding benzaldehyde derivative (**14**) in 76% yield. The silyl based template can act as a nucleophile in presence of TBAF. To demonstrate that, 4-nitrobenzaldehyde (**15**) and 2-naphthaldehyde (**17**) was treated with *para*-olefinated product **2e** and **6c**, respectively to produce corresponding benzyl alcohols (**16** and **18** in 83% and 72%, respectively).

Table 4 Scope of α-substituted toluene derivatives and more complex olefin coupling partners[a][11]

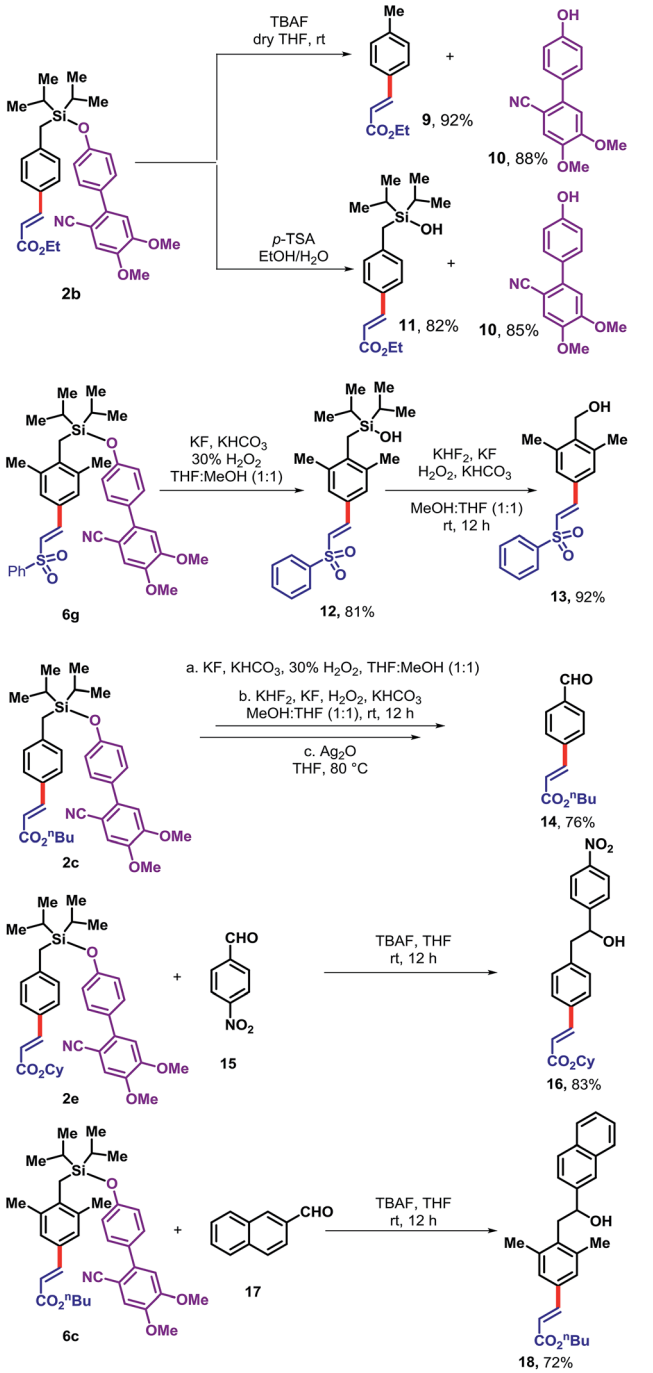


[a] Ratio of *para*: others determined by the ^{1}H NMR of crude reaction mixture.

Isotope labeling experiments were conducted involving an intermolecular competition using substrate **1a** and its deuterated analogue D$_7$-**1a** and a P_H/P_D value of 2.9 and k_H/k_D value of 2.6 were obtained (Scheme 4).[11] Furthermore, a detailed kinetic study indicated that the reaction was first order with respect to the substrate and zero order with respect to the olefin.[11] Together, these results suggest that the C–H bond activation is likely to be the rate-determining step of the catalytic cycle. A plausible catalytic cycle for the *para*-olefination is shown in Scheme 5. In this mechanism, the Rh(I) catalyst precursor is first oxidized to Rh(III). The main steps in the cycle consist of C–H activation, migratory insertion, β-hydride elimination, and reductive elimination.[11]

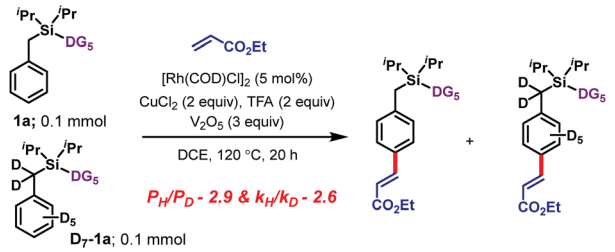
We explored the C–H activation process using density functional theory (DFT) (Fig. 1). Computations with the M06 functional using a model of **DG$_1$** with trifluoroacetate anion as the base predicted that the C–H bond activation follows an electrophilic aromatic substitution pathway, with a distinct intermediate **Int1**, rather than a concerted metalation–deprotonation pathway.[10p,12] Transition structures for C–H bond breaking at the *para* and *meta* positions are shown in Fig. 1.

The *para* transition state, **TS1-*para***, is 6.5 kcal mol^{-1} lower in energy than the *meta* transition state **TS1-*meta***. A fragment-based analysis of the TSs[12] reveals that the preference for *para*-C–H activation is due to a β-silicon effect. The interaction of the arene with Rh(III) endows it with arenium cation character, and this interaction is strengthened in **TS1-*para*** because

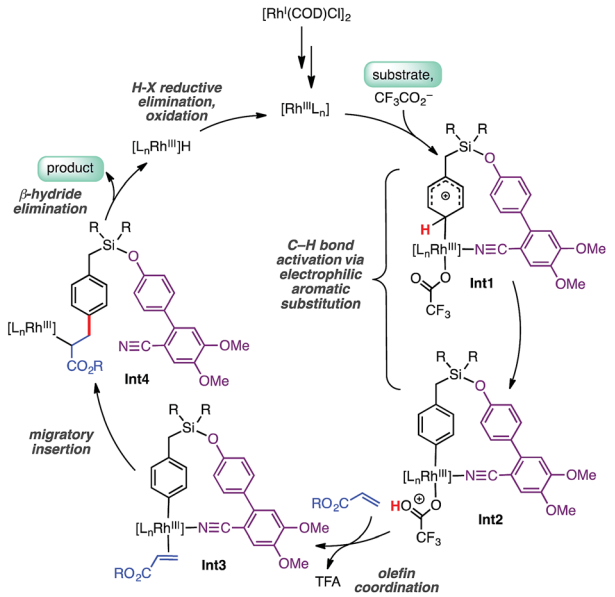


Scheme 3 Removal of the directing group and diversification of the *para*-olefinated products.[11]

the C–Si bond (which lies perpendicular to the ring) stabilizes the positive charge through hyperconjugation. Computations also revealed the roles of the DG methoxy and nitrile substituents.[12] Incorporation of two methoxy groups on the DG activates the substrate toward C–H bond breaking, lowering the barrier by 1.6 kcal mol^{-1} relative to **TS1-*para***. A TS in which the nitrile is not bound to Rh was computed to be 23 kcal mol^{-1} higher in energy than **TS1-*para***, indicating that the coordination of the nitrile to Rh strongly stabilizes the C–H activation transition state.



Scheme 4 Experiments with a deuterium-labeled substrate.[11]



Scheme 5 Possible catalytic cycle for *para*-selective Rh-catalyzed olefination.

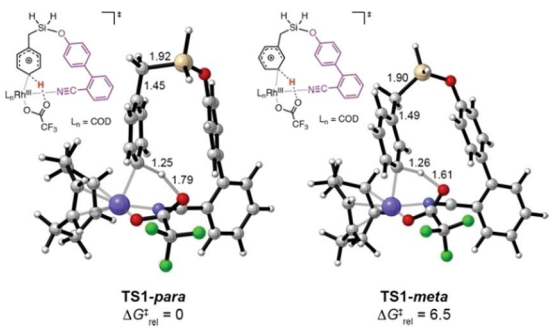


Fig. 1 Transition states for Rh(III)-mediated *para*-C–H and *meta*-C–H bond activation, computed with M06/6-311+G(d,p)-SDD//M06/6-31G(d,p)-LANL2DZ in SMD dichloroethane. Distances in Å, $\Delta G^{\ddagger}_{rel}$ in kcal mol^{-1}.

Conclusions

In summary, herein we have reported the first example of a Rh-catalyzed distal *para*-C–H functionalization reaction. The Rh-catalyzed olefination of toluenes using the Si-linked **DG$_5$** directing group displays broad substrate tolerance. Electron-rich and electron-deficient arenes are coupled with electron-deficient olefins in high yield and selectivity. Mechanistic studies are consistent with a catalytic cycle in which the C–H bond activation is rate-determining. This work reveals the potential of Rh catalysis to diversify the scope of functionalizations in the realm of remote *para*-C–H activation.

Conflicts of interest

The authors declare no conflict of interest.

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11 See the ESI† for detailed descriptions.

12 We also considered several other mechanisms in which the CH bond cleavage step is mediated by either Rh(III) or Rh(I), details are provided in the ESI.†