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Rh-Catalyzed C−C Cleavage of Benzyl/Allylic Alcohols to Produce Benzyl/Allylic Amines or other Alcohols by Nucleophilic Addition of Intermediate Rhodacycles to Aldehydes and Imines

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Abstract: We report three transformations: 1) direct transformation from biarylmethanols into biarylmethylamines; 2) direct transformation from one biarylmethanol into another biarylmethanol; 3) direct transformation from allylic alcohols into allylic amines. These transformations are based on pyridyl-directed Rh-catalyzed C−C bond cleavage of secondary alcohols and subsequent addition to C=X (X = N or O) double bonds. The reaction conditions are simple and no additive is required. The driving force of C−C bond cleavage is the formation of the stable rhodacycle intermediate. Other directing groups, such as the pyrazolyl group, can also be used although it is not as efficient as the pyridyl group. We carried out in-depth investigations for transformation 1 and found that: 1) the substrate scope was broad and electron-rich alcohols and electron-deficient imines are more efficient; 2) as the leaving group, aldehyde had no significant impact on either the C−C bond cleavage or the whole transformation; 3) mechanistic studies (intermediate isolation, in situ NMR spectroscopic studies, competing reactions, isotopic labeling experiments) implied that: i) The C−C cleavage was very efficient under these conditions; ii) there is an equilibrium between the rhodacycle intermediate and the protonated byproduct phenylpyridine; iii) the addition step of the rhodacycle intermediate to imines was slower than the C−C cleavage and the equilibrium between the rhodacycle and phenylpyridine; iv) the whole transformation was a combination of two sequences of C−C cleavage/nucleophilic addition and C−C cleavage/protonation/C−H activation/nucleophilic addition, with the latter being perhaps the main pathway. We also demonstrated the first example of cleavage of an C(alkenyl)−C(benzyl) bond. These transformations showed the exchange (or substitution) of the alcohol group with either an amine or another alcohol group. Like the "group transplant", this method offers a new concept that can be used to directly synthesize the desired products from other chemicals through reorganization of carbon skeletons.

Keywords: allylic compounds · C−C activation · rhodium · alcohols · synthetic methods

Introduction

The nucleophilic addition of organometallic reagents to C=X double bonds (X = O, N) is an important method that can be used to synthesize alcohols and amines, which are important compounds in organic synthesis. For example, Grignard reagents[1] and organolithium reagents[2] are widely used in nucleophilic addition to C=X double bonds. However, these reagents suffer from air- and moisture-sensitivity. Organoboron reagents can also be used as nucleophiles in the addition to C=X bonds in the presence of a metal catalyst, for example Rh,[3] Pd,[4] Fe,[5] Ni,[6] Ru,[7] Co,[8] Cu,[9] and Pt.[10] However, most of these organometallic reagents are prepared from environmentally unfriendly and expensive organohalides. Organohalides can also be directly used as nucleophiles in the addition to C=X bonds catalyzed by metal species.[11] Recently, carboxylic acids have been shown to undergo nucleophilic addition to C=X bonds through decarboxylation.[12] Direct C−H bond addition to the C=X bonds has also been achieved and is more efficient and atom economic.[13] Especially, Rh catalysis has played an important role in this field.[14–20] In addition, Rh catalysts have also been used in other types of C−H functionalization reactions.[21–23] These transformations are relatively benign to the environment.

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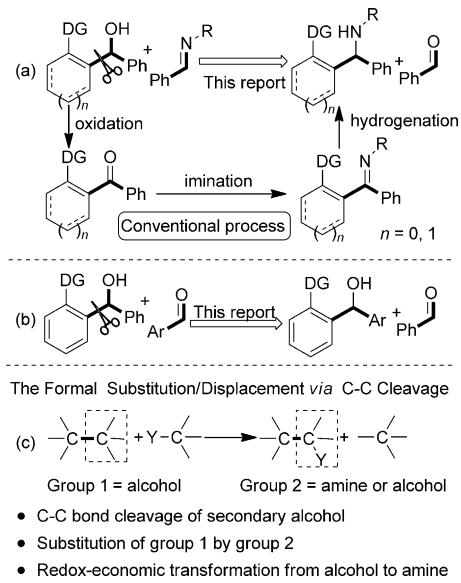
Another type of ubiquitous inert bond besides C–H bonds are C–C bonds. Similar to the process of catalytic C–H addition to C=X bonds, in which an organometallic intermediate (C–M bond) was produced by C–H activation, C–C bond activation can also produce the active organometallic intermediate (C–M bond) and proceed through subsequent addition reaction with the C=X bonds. Based on our interest in C–C bond activation,[24] here we set out to investigate the reactivity of C–C bonds towards addition to C=X bonds. In contrast to C–H addition to C=X bonds, the addition reaction by C–C activation has been less extensively investigated. Oshima and Yorimitsu reported the allyl transfer reaction from homoallyl alcohols to aldehydes through retro-allylation, but the alcohol could not be obtained because of isomerization to the aldehyde.[25] Later, Oshima and Yorimitsu reported the Cu-catalyzed C–C bond cleavage of tertiary alcohols and subsequent addition to aldehydes and imines.[26] Herein, we report the Rh-catalyzed $C_{(aryl)}$–$C_{(benzyl)}$ and $C_{(alkenyl)}$–$C_{(benzyl)}$ bond cleavage of secondary alcohols and subsequent addition to imines and aldehydes (Scheme 1). First, we realized the transformation



Scheme 1. Formal group substitution/displacement through Rh-catalyzed C–C cleavage.

from benzyl and allylic alcohol into amine by replacing the aldehyde with an imine through Rh-catalyzed C–C bond cleavage/nucleophilic addition (Scheme 1, a). In general, such a process requires multi-step redox transformations (Scheme 1, a), although recent advances have realized the alcohol–amine transformation by the hydrogen-borrowing-lending strategy in one pot without scaffold reorganization.[27] In addition, we expanded this strategy to the transformation from benzyl alcohol into another benzyl alcohol by replacing one aldehyde with another aldehyde through Rh-catalyzed C–C bond cleavage/nucleophilic addition (Scheme 1, b). Formally, this kind of transformation is a direct group substitution (displacement) reaction through cleavage of a C–C single bond (Scheme 1, c).[28]

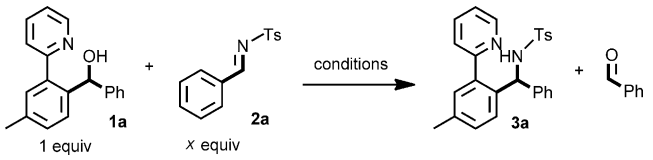
Through the sequence of C–C bond cleavage and C–C bond formation, the organic skeleton can be reorganized, which may provide an efficient method to construct complex molecules from widely existing organic compounds as starting materials.[29] Despite the promising applications of this sequence of C–C bond cleavage and subsequent C–C bond formation, the C–C cleavage faces several challenges: 1) the high bond dissociation energy of C–C bonds,[30] 2) the difficult approach of the metal center to C–C bonds,[31] and 3) the poor selectivity associated with C–C activation.[32] Several strategies (release of ring strain,[33] formation of stable metallacycle or π-allyl metal complex as intermediates in the assistance of coordination,[34] formation of stable C–metal bonds,[35] and others[36]) have been adopted to realize the C–C activation and subsequent organic transformations.

In contrast to tertiary alcohols, the C–C bond cleavage of secondary alcohols is much more challenging, resulting from the oxidation reaction to give ketones (β-H elimination)[37] competing with the C–C activation reaction (β-C elimination).[38] In our previously developed C–C activation[24a] and C–H addition,[15b] we investigated the reaction mechanism and identified the rhodacycle intermediate, which has a transformable C–Rh bond. Based on these analyses, we selected secondary alcohol **1a** as our model substrate. The C–C activation in this substrate was believed to be driven by the pyridyl directing group.

Results and Discussion

Transformation from benzyl alcohol into benzyl amine: Conditions: Secondary alcohol **1a** and *N*-sulfonylimine **2a** were selected as model substrates to establish optimal conditions to achieve this transformation (Table 1). Because of the wide use of Rh catalysts in the C–C activation reaction,[39–46] Rh catalysts were first selected and investigated. Although $[Cp^*RhCl_2]_2$ showed good catalytic activity in the C–C cleavage in our previous studies,[24a] group substitution leading to the desired product **3a** was not observed (Table 1, entry 1). However, to our delight, when $[Cp^*Rh(CH_3CN)_3][SbF_6]_2$ was used as a catalyst, the desired product **3a** was obtained in 38% yield (Table 1, entry 2). Increasing the concentration of **1a** from 0.05 to 0.20 M resulted in a better yield of 67% (Table 1, entry 4). The yield was clearly enhanced when 3.0 equivalent of **2a** was presented (Table 1, entry 5); further improvement could not be reached by further increasing the amount of **2a** or the concentration (Table 1, entries 6 and 7). Reducing the reaction time gave a similar result (Table 1, entry 8). Lower temperature suppressed the efficiency, whereas higher temperature did not lead to a better outcome (cf. Table 1, entries 8–10). Notably, this transformation did not proceed in the presence of other transition metal catalysts or in the absence of catalyst (Table 1, entries 11–18). Among various solvents, *t*BuOH

Table 1. Screening of Rh^{III}-catalyzed C–C bond cleavage/addition of secondary alcohol **1a** with imine **2a**.



Entry	Conc. [M]	x	Cat. (5 mol%)	T [°C]	Solvent [(1 mL)]	t [h]	Yield [%][a]
1[b]	0.05	2	$[Cp^*RhCl_2]_2$	90	*t*BuOH	10	0
2	0.05	2	$[Cp^*Rh(CH_3CN)_3][SbF_6]_2$	90	*t*BuOH	10	38
3	0.10	2	$[Cp^*Rh(CH_3CN)_3][SbF_6]_2$	90	*t*BuOH	10	63
4	0.20	2	$[Cp^*Rh(CH_3CN)_3][SbF_6]_2$	90	*t*BuOH	10	67
5	0.20	3	$[Cp^*Rh(CH_3CN)_3][SbF_6]_2$	90	*t*BuOH	10	79
6	0.20	4	$[Cp^*Rh(CH_3CN)_3][SbF_6]_2$	90	*t*BuOH	10	77
7	0.25	3	$[Cp^*Rh(CH_3CN)_3][SbF_6]_2$	90	*t*BuOH	10	75
8	0.20	3	$[Cp^*Rh(CH_3CN)_3][SbF_6]_2$	90	*t*BuOH	3	77
9	0.20	3	$[Cp^*Rh(CH_3CN)_3][SbF_6]_2$	60	*t*BuOH	3	11
10	0.20	3	$[Cp^*Rh(CH_3CN)_3][SbF_6]_2$	120	*t*BuOH	3	80
11	0.20	3	$Pd(OAc)_2$	90	*t*BuOH	3	0
12	0.20	3	$Cu(OAc)_2$	90	*t*BuOH	3	0
13	0.20	3	$Fe(acac)_3$	90	*t*BuOH	3	0
14	0.20	3	$Ni(acac)_2$	90	*t*BuOH	3	0
15	0.20	3	$[Rh(COD)OH]_2$	90	*t*BuOH	3	0
16	0.20	3	$(PPh_3)_3RhCl$	90	*t*BuOH	3	0
17	0.20	3	$Rh(acac)_3$	90	*t*BuOH	3	0
18	0.20	3	No	90	*t*BuOH	3	0
19	0.20	3	$[Cp^*Rh(CH_3CN)_3][SbF_6]_2$	90	EtOH	3	60
20	0.20	3	$[Cp^*Rh(CH_3CN)_3][SbF_6]_2$	90	*t*AmylOH	3	55
21	0.20	3	$[Cp^*Rh(CH_3CN)_3][SbF_6]_2$	90	*i*PrOH	3	64
22	0.20	3	$[Cp^*Rh(CH_3CN)_3][SbF_6]_2$	90	THF	3	46
23	0.20	3	$[Cp^*Rh(CH_3CN)_3][SbF_6]_2$	90	dioxane	3	52
24	0.20	3	$[Cp^*Rh(CH_3CN)_3][SbF_6]_2$	90	DCE	3	48
25	0.20	3	$[Cp^*Rh(CH_3CN)_3][SbF_6]_2$	90	toluene	3	53

[a] Isolated yields are given unless otherwise noted. [b] 2.5 mol% of catalyst.

was found to be the most effective (Table 1, entries 19–25). In general, protic solvents were better than nonprotic solvents in terms of efficiency.

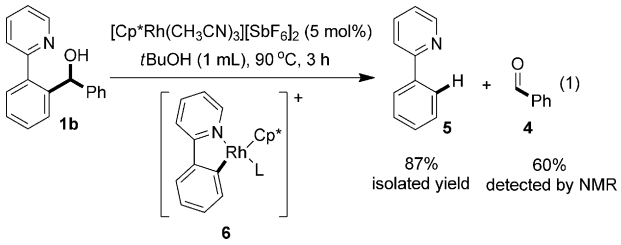
Transformation from benzyl alcohol into benzyl amine: Substrate scope of alcohols: With these optimized conditions in hand, we began to explore the substrate scope of different alcohols (Table 2). To our delight, the *para*-methyl substituent was not necessary for promoting the efficiency and selectivity. We found that nonsubstituted substrate **1b** gave a comparable yield to that obtained with **1a**. Electron-donating and electron-withdrawing groups on the phenyl motif (**1c**–**f**, and **1h**) can be tolerated in this system, although electron-deficient substrates (**1e** and **1h**) gave relatively lower yield, which could be attributed to the lower nucleophilicity of the rhodacycle intermediate towards addition to imine. Halogen-containing substrates (**1e**) can also be tolerated, affording the possibility for further transformations.[47]

Different functionalities on the phenyl ring of the leaving group were also tested. Neither electron-rich nor electron-deficient leaving groups (**1i** and **1j**) affected the efficiency dramatically. Alkyl alcohols **1k** and **1l** also successfully underwent the desired C–C cleavage/nucleophilic addition sequence, although the efficiency was not comparable with biaryl methanols. In addition to secondary alcohols, tertiary alcohol **1n** was tested and we found that group transfer also took place with good efficiency. Remarkably, primary alcohol **1m** showed partial reactivity, with significant amounts of starting material remaining. The low efficiency probably results from the thermodynamic stability of the C–C bond in this substrate and the difficulty in forming the five-member rhodacycle. Moreover, substrates containing two alcoholic structural units (**1o**, **1p** and **1q**) were further tested, and the results indicated that the transformation for such substrates showed high regio- and chemo-selectivity; only the alcohol group adjacent to the pyridyl group showed good reactivity and different alcohol groups (primary, secondary, and tertiary) at the *meta*-position were untouched. Secondary alcohol substitution resulted in lower yield, possibly arising from oxidation of this functional group (**1p**). In the presence of a tertiary alcohol group (**1q**), the desired product **3qa** was obtained in 60% yield, accompanied by 28% yield of **3qa′** formed from further dehydration of the tertiary alcohol group.

Transformation from benzyl alcohol into benzyl amine: Substrate scope of imines: A range of sulfonylaldimines were further investigated (Table 3), and it was found that the reaction was very sensitive towards steric effects. For example, although imines with methyl groups at the *meta*- and *para*-positions of the phenyl group underwent this reaction smoothly, those with an *ortho*-methyl substituent decreased the yield significantly (cf. **3bb** and **3bc** with **3bd**). The presence of electron-withdrawing groups significantly improved the yields (**3be**, **3bf**, **3bi**, **3bj**, and **3bk**), which can be rationalized by the higher electrophilicity of the corresponding imines. In contrast, substrates with an electron-donating group afforded the product in much lower yield (**3bl**). It should be noted that halogen-containing imines were tolerated well in this catalytic system, making it possible for further orthogonal transformations (**3bg**, **3bh**). In addition, naphthyl, biphenyl, and heteroaromatic ring containing imines were also suitable electrophiles for this transformation (**3bm**, **3bn**, and **3bo**). Finally, protecting groups of imines other than the tosyl group were tested and both (4-fluorophenyl)sulfonyl (Fs) and methanesulfonyl (Ms) were found to be suitable for this transformation (**3bp**, **3bq**). The higher yield of **3bp** (than **3bq**) results from the stronger electrophilicity of 4-fluorophenylsulfonylimine. We also assessed the use of the pyrazolyl group as the directing group but found that, although the desired product was obtained, its yield was low (**3ra**).

Transformation from benzyl alcohol into benzyl amine: Mechanistic investigations: To gain insights into the mechanism, we conducted this reaction in the absence of imine partner **2** under standard conditions to investigate the C–C

cleavage step [Eq. (1)]. The C–C bond cleavage indeed took place and 2-phenylpyridine (**5**) was obtained in 87% yield together with benzaldehyde (**4**) as leaving group in 60% yield. This result proved that the C–C bond was cleaved and that **5** may result from further protonation of the five-membered rhodacycle **6**. Therefore, further experiments were conducted to determine whether the five-membered rhodacycle **6** was involved in our system and acted as key intermediate. Unfortunately, although the starting material was consumed in the stoichiometric reaction between alcohol and catalyst, pure compound **6** could not be separated due to contamination by $HSbF_6$ salts of the 2-phenylpyridine byproduct. However, intermediate **6** was identified by ESI-MS analysis (see the Supporting Information). Fortunately, intermediate **6**, prepared by another method,[16b] was found to efficiently catalyze this reaction [Eq. (2)], indicating that this



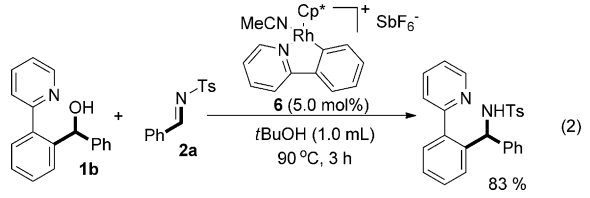
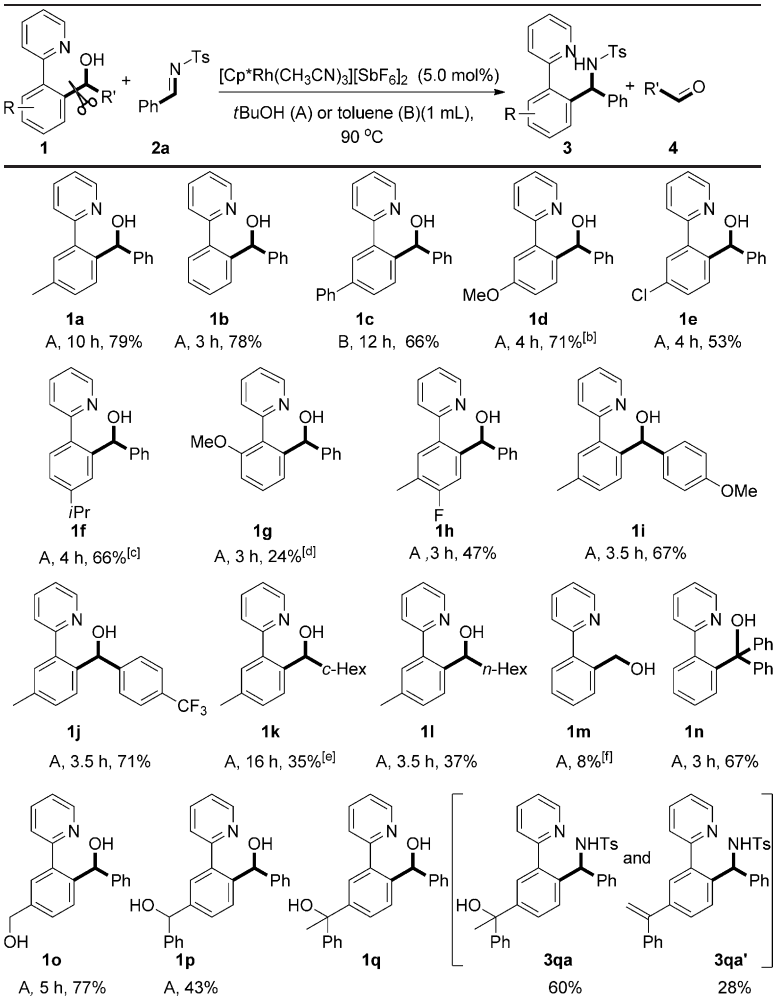


Table 2. Rh^{III}-catalyzed addition of secondary alcohols **1** with **2a** through C–C bond cleavage.[a]



[a] Reagents and conditions (0.2 mmol scale): alcohol **1**, $[Cp^*Rh(CH_3CN)_3][SbF_6]_2$ (5 mol%), imine (3 equiv), *t*BuOH (1.0 mL; conditions A) or toluene (1.0 mL; conditions B), unless otherwise noted. Isolated yields are shown in the table. [b] 1.5 mL *t*BuOH. [c] 0.5 mmol scale, 2.5 mL *t*BuOH. [d] With 59% 2-(2-methoxyphenyl)pyridine formed as a byproduct. [e] 0.15 mmol scale, 1 mL *t*BuOH. [f] Reacted at 90 °C for 24 h, then at 120 °C for 19 h; significant amounts of starting material remained; the yield was determined by NMR spectroscopic analysis.

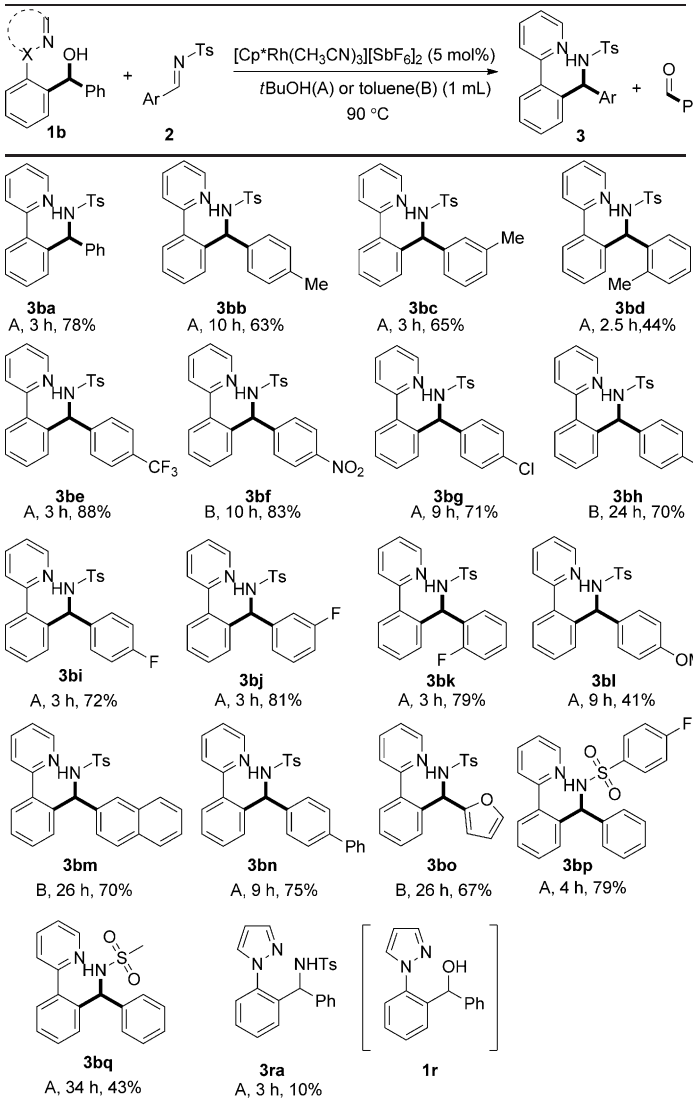
five-membered rhodacycle intermediate was actually involved in our catalytic cycle.

Next, we investigated the addition step from intermediate **6** to the final product. For this step, there may be two different pathways: Path A, the C–C cleavage/direct addition sequence, and Path B, the C–C cleavage/protonation/C–H activation cascade sequence (Scheme 2).

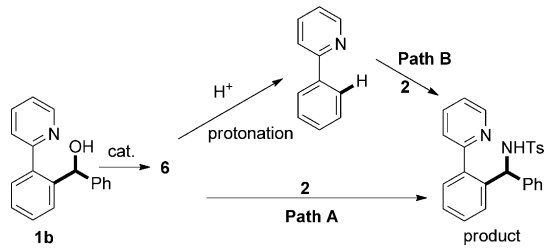
First, we used in situ NMR experiments to detect the trend of change in concentration (yields) of starting material **1**, desired product **3**, and possible intermediate **5** (Figure 1). At the initial stage of the reaction, the concentration of alcohol **1b** decreased sharply, companying the formation of large amounts of 2-phenylpyridine **5**. After 1.5 h, most of the starting material **1b** was consumed and transformed into the desired imine **3ba** (ca. 10% yields) and the protonated byproduct **5**. With further time, the concentration of **5** gradually decreased and the yield of product continued to increase. Complete conversion was not achieved due to the lower concentration under the NMR conditions (see the Supporting Information). Several conclusions could be drawn from this data: 1) The C–C cleavage was very efficient under these conditions; 2) There is an equilibrium between the rhodacycle intermediate **6** and the protonated byproduct **5**; 3) The addition step of the intermediate **6** to imine **2** was slower than the C–C cleavage and the equilibrium between **6** and **5**, so most of the starting material alcohol was transformed into **5** during the reaction; 4) Path B was the main pathway but Path A was also involved, because the rate of increase of the product was higher at the initial stage than later.

We further conducted several other experiments to support the conclusions mentioned above. A competition experiment between **5** and **1a** was carried out. To our interest, **3ba** and **3aa** were obtained in comparable yields, indicating that pathway B was the main route to the desired product

Table 3. Rh^{III}-catalyzed addition of **1b** with imines through C–C bond cleavage.[a]

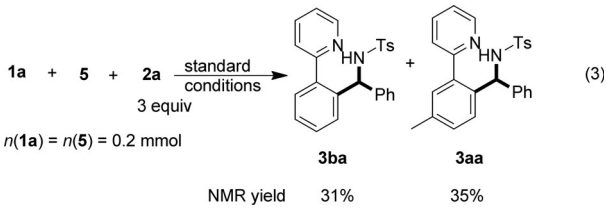


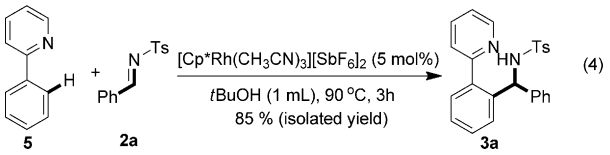
[a] Reagents and conditions (0.2 mmol scale): alcohol **1**, $[Cp^*Rh(CH_3CN)_3][SbF_6]_2$ (5 mol%), imine (3 equiv), *t*BuOH (1.0 mL; conditions A) or toluene (1.0 mL; conditions B). Isolated yields are shown in the table.



Scheme 2. Two different pathways.

[Eq. (3)]. Indeed, the addition of a C–H bond to sulfonylaldimine took place under exactly the same conditions [(Eq. 4)].





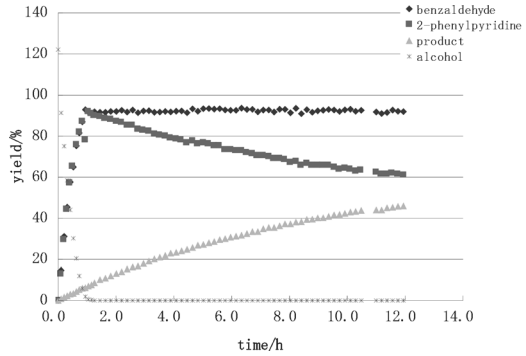
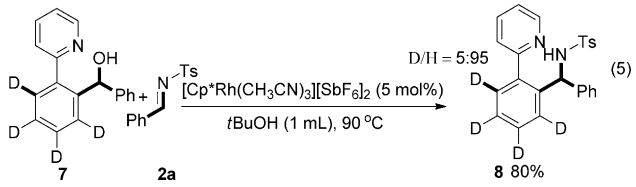
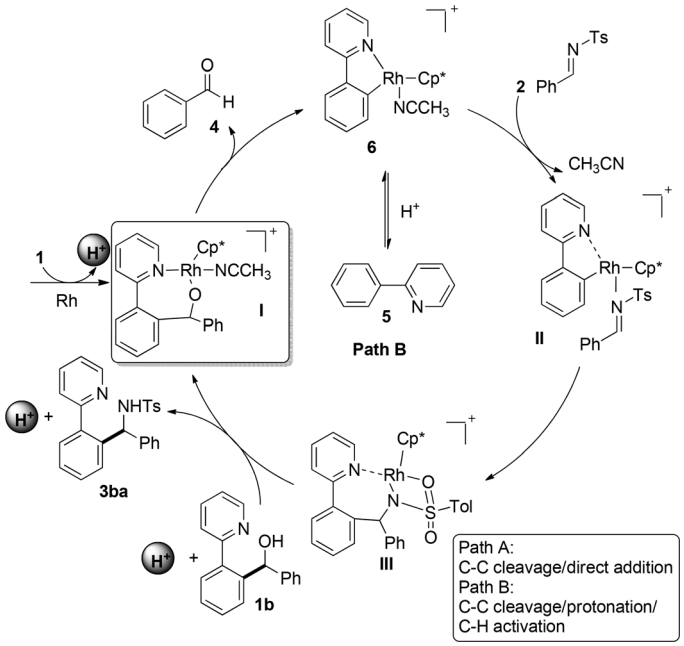


Figure 1. In situ NMR spectroscopic analysis; the relationship between the concentrations of the product, starting material alcohol, and phenylpyridine **5** and reaction time.

To further clarify this issue, an isotopic labeling experiment was carried out. We found that, other than the group transplant to form amines, D/H scrambling took place at the *ortho*-position, indicating that the C–H cleavage was accompanied by C–C cleavage under these conditions [Eq. (5)]. Notably, the high value of the H/D ratio implied that C–H activation was reversible to some extent, which is in accordance with our conclusion from the in situ NMR spectroscopic study that there is an equilibrium between the rhodacycle intermediate **6** and the protonated byproduct 2-phenylpyridine **5**. These observations suggested that both the C–C cleavage/direct C–C formation and the sequence of C–C cleavage/protonation/C–H activation/C–C formation existed under the reaction conditions and that Path B was the main route to the resulting group substitution/displacement.



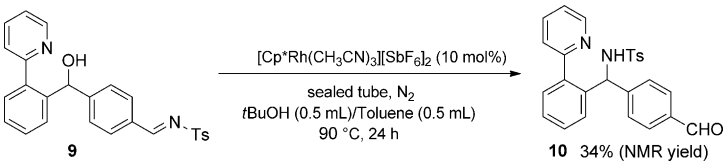
Based on these experimental results, we proposed that this transformation proceeds through the pathway shown in Scheme 3. First, the precatalyst coordinates with substrate



Scheme 3. Proposed mechanism.

1b to form seven-membered rhodacycle intermediate **I**, releasing a proton to the reaction mixture. Subsequent β-C elimination accompanied by release of benzaldehyde **4** gave five-membered rhodacycle intermediate **6**, which can either undergo direct addition with imines (Path A) to give the desired product or undergo the protonation process to generate the 2-phenylpyridine derivative **5** (Path B). The 2-phenylpyridine derivative **5** can also give the desired product through the C–H activation process.[15b]

Formal intramolecular reaction: To make this reaction a 100% atom economic reaction, one should avoid the release of the benzaldehyde as a leaving group. Based on this idea, we synthesized substrate **9** for an intramolecular reaction, which reacted efficiently under these conditions to give the alcohol–amine exchange product **10** in 34% NMR yield (Scheme 4).

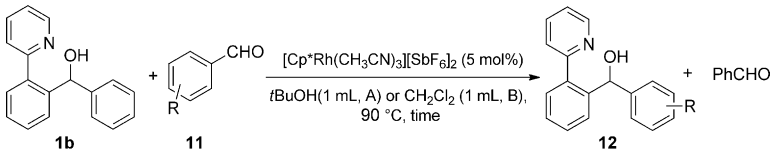


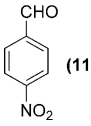
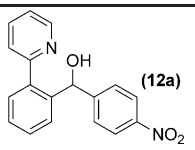
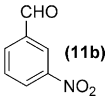
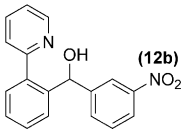
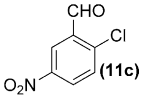
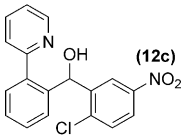
Scheme 4. Alcohol–amine exchange reaction.

Transformation between alcohol groups: Interestingly, the alcohol group can not only be substituted by amine groups, but also by other alcohol groups, realizing the transformation from one alcohol into another alcohol (Table 4).[18] Here, the electrophilic partner aldehyde **11** should contain an electron-withdrawing group and thus be more electrophilic than benzaldehyde because, actually, this is a competing reaction between two different aldehydes toward the same nucleophilic metal intermediate. 4-Nitrobenzaldehyde (**11a**) and 2-chloro-5-nitrobenzaldeyde (**11c**) showed better efficiency than 3-nitrobenzaldehyde (**11b**). It was found that dichloromethane was a better solvent than *t*BuOH for this transformation. In summary, this reaction demonstrated the versatility of the substitution reaction through C–C cleavage.

Transformation from allylic alcohol into allylic amine: Having realized the reaction between benzyl alcohols with imines, we continued to investigate the reaction between allylic alcohols and imines. Gratifyingly, the C(alkenyl)–C(benzyl) bond was cleaved and the desired allylic amine product was obtained in moderate yields (Table 5). To the best of our knowledge, this is the first report of the cleavage of an C(alkenyl)–C(benzyl) bond. Longer reaction time and higher temperature had no effect on the yield (Table 5,

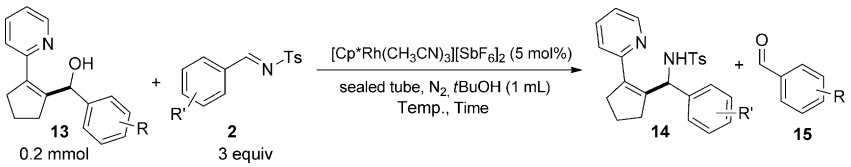
Table 4. The substitution of one alcohol group with a second.[a]

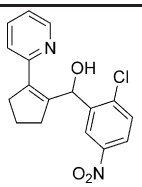
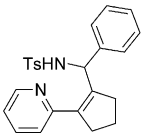
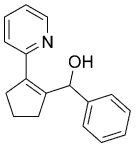
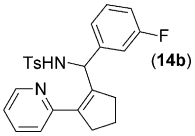


Entry	Alcohol **11**	Product **12**	Solvent	Time [h]	Yield [%]
1	 **(11a)**	 **(12a)**	A	24	47
2[b]	**11a**	**12a**	B	20	61
3	 **(11b)**	 **(12b)**	B	24	24
4	 **(11c)**	 **(12c)**	A	3	57
5	**11c**	**12c**	B	24	71

[a] Reagents and conditions (0.2 mmol scale): alcohol **1b**, $[Cp^*Rh(CH_3CN)_3][SbF_6]_2$ (5 mol%), aldehyde **11** (3 equiv), *t*BuOH (1.0 mL; conditions A) or CH_2Cl_2 (1.0 mL; conditions B), unless otherwise noted. Isolated yields are shown in the table. [b] Reaction conducted on a 0.1 mmol scale in 0.5 mL CH_2Cl_2.

Table 5. The reaction between allylic alcohols and imines to produce allylic amines.[a]



Entry	Allylic alcohol **13**	Product allylic amine **14**	*T* [°C]	*t* [h]	Yield [%]
1	 **(13a)**	 **(14a)**	90	3	42[b]
2	**13a**	**14a**	110	48	46
3	 **(13b)**	**14a**	110	52	47
4	**13a**	 **(14b)**	110	48	47
5[c]	**13b**	**14b**	110	48	45

[a] Reagents and conditions (0.2 mmol scale): substrate **13**, $[Cp^*Rh(CH_3CN)_3][SbF_6]_2$ (5 mol%), imine **2** (3 equiv), *t*BuOH (1.0 mL), unless otherwise noted. Isolated yields are shown in the table. [b] NMR yield with 21% starting material alkene remaining. [c] PivOH (20 mol%) was added and *t*BuOH (0.5 mL) and CH_2Cl_2 (0.5 mL) were used as the solvent.

entry 2), indicating that there was an equilibrium formed during the reaction resulting from the competition between imine **2a** and the released aldehyde **15** to be nucleophilicly attacked by the Rh intermediate (Table 5, entries 2 vs. 1). In addition, different leaving groups (Table 5, entries 2 vs. 3) and different imines (Table 5, entries 2 vs. 4) had no significant impact on the yield.

Conclusion

The pyridylphenyl-group transfer reaction, the direct transformation from secondary alcohols, tertiary alcohols and even primary alcohols into biarylmethylamines through a Rh^{III}-catalyzed carbon–carbon cleavage/carbon–carbon formation sequence, was developed. The reaction is straightforward to perform and no additive is required. The functional group tolerance is good and electron-rich alcohols and electron-deficient imines are better in efficiency. The electronic nature of the leaving group has no significant impact on the yield. The mechanism is a combination of C–C cleavage/addition (Path A) and C–C cleavage/protonation/C–H activation/addition (Path B), with the latter being the main route. Mechanistic studies showed that: 1) the C–C cleavage was very efficient under these conditions; 2) there is an equilibrium between the rhodacycle intermediate **6** and the protonated byproduct 2-phenylpyridine **5**; 3) the addition step of the intermediate **6** to imine **2** was slower than the C–C cleavage and the equilibrium between **6** and **5**.

We also realized the direct transformation from one secondary benzyl alcohol into another benzyl alcohol and the first pyridylcyclopentenyl-group transfer reaction, the direct transformation from secondary allylic alcohols into allylic amines through Rh^{III}-catalyzed carbon–carbon cleavage/carbon–carbon formation sequence.

Through these reactions, we investigated the reactivities of C–C bond addition to aldehydes and imines. In addition, as a substitution reaction proceeding through C–C bond cleavage, this method offers a concept that can be used to synthesize the desired products through direct reorganization of carbon skeletons. These studies are not only theoretically important to understand the new reactivity of traditionally considered "inert" compounds, but also potentially synthetically useful for the construction of valuable chemicals from readily available and inexpensive chemicals. Further investigations to explore new transformations using this substitution strategy through C–C bond cleavage is underway. Investigation of the application of this strategy in the degradation of "white pollutants" is also our goal.

Experimental Section

General procedures: *Synthesis of alcohols* **1**: The procedure for the synthesis of the alcohols was the same as that reported by our group recently.[16] Alcohol substrates **1a–c**, **1e**, **1f**, **1k–n, 1p–r**, and **7** were included in the literature[16] and the characterization data are consistent with reported data. Alcohol substrates **1d**, **1g–j**, and **1o** were not reported and were synthesized according to the literature method.[16]

Synthesis of **3**: A 50 mL Schlenk tube was heated using a heat gun under vacuum. After cooling to RT, catalyst $[Cp^*Rh(CH_3CN)_3][SbF_6]_2$ (8.3 mg, 0.01 mmol), alcohol derivative **1** (0.2 mmol), and aldimine derivative **2** (0.60 mmol) were added under air atmosphere. The reaction tube was then evacuated and refilled with N_2. After the addition of freshly distilled *t*BuOH (1.0–2.5 mL) or toluene (1.0–2.5 mL) by using a syringe, the reaction mixture was stirred in the sealed tube at 90°C under N_2 atmosphere in a Wattecs Parallel Reactor for the time indicated (reaction monitored by TLC to achieve full conversion of **1** and better yield of the product **3**). After cooling to RT, the solvent was removed in vacuo and the residue

was purified by chromatography on silica gel (petroleum ether/EtOAc, 6:1 to 2:1, or petroleum ether/EtOAc/CH_2Cl_2, 6:1:1 to 3:1:1) to afford compound **3** as a white solid.

Compound 3aa (the same product as **3ia**, **3ja**, **3ka**, and **3la**): Obtained as a white solid after column chromatography (petroleum ether/ethyl acetate/CH_2Cl_2, 6:1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.75 (d, J = 8.8 Hz, 1H), 8.52–8.50 (m, 1H), 7.60 (d, J = 8.8 Hz, 2H), 7.43 (dt, J = 1.6, 7.6 Hz, 1H), 7.07–7.02 (m, 4H), 6.93–6.89 (m, 8H), 5.66 (d, J = 9.2 Hz, 1H), 2.33 (s, 3H), 2.31 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.0, 147.4, 142.2, 140.9, 139.2, 138.8, 137.4, 136.9, 136.8, 132.0, 131.1, 129.0, 128.7, 127.3, 126.9, 126.1, 126.0, 124.3, 121.8, 61.1, 21.3, 20.9 ppm; HRMS (ESI): m/z calcd for $C_{26}H_{25}N_2O_2S$: 429.16313 $[M+H]^+$; found: 429.16321.

Compound 3ca: Obtained as a white solid by column chromatography (petroleum ether/ethyl acetate/CH_2Cl_2, 5:1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.86 (d, J = 12 Hz, 1H), 8.55–8.53 (m, 1H), 7.64–7.61 (m, 2H), 7.55–7.52 (m, 2H), 7.47–7.41 (m, 4H), 7.39–7.36 (m, 1H), 7.29–7.26 (m, 1H), 7.10–6.92 (m, 10H), 5.75 (d, J = 12.0 Hz, 1H), 2.24 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.8, 147.6, 142.3, 140.7, 140.6, 140.0, 139.8, 138.9, 138.7, 137.0, 131.6, 130.1, 129.0, 128.8, 127.6, 127.4, 126.9, 126.6, 126.3, 126.0, 124.5, 122.0, 61.2, 21.3 ppm; HRMS (ESI): m/z calcd for $C_{31}H_{27}N_2O_2S$: 491.17878 $[M+H]^+$; found: 491.17881.

Compound 3da: Obtained as a white solid by column chromatography (petroleum ether/ethyl acetate/CH_2Cl_2, 5:1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.71 (d, J = 12 Hz, 1H), 8.52–8.50 (m, 1H), 7.61 (d, J = 9.0 Hz, 2H), 7.44 (dt, J = 3.0, 9.0 Hz, 1H), 7.09–7.05 (m, 3H), 7.01–6.89 (m, 7H), 6.75 (d, J = 3.0 Hz, 1H), 6.57 (dd, J = 3.0, 9.0 Hz, 1H), 5.64 (d, J = 12.0 Hz, 1H), 3.77 (s, 3H), 2.33 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.5, 158.8, 147.5, 142.2, 141.0, 140.6, 138.8, 137.0, 132.3, 132.2, 129.0, 127.3, 126.9, 126.0, 125.9, 124.3, 122.0, 117.4, 112.6, 60.7, 55.3, 21.3 ppm; HRMS (ESI): m/z calcd for $C_{26}H_{25}N_2O_3S$: 445.15804 $[M+H]^+$; found: 445.15830.

Compound 3ea: Obtained as a white solid (light-pink) by column chromatography (petroleum ether/ethyl acetate/CH_2Cl_2, 5:1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.63 (d, J = 9.6 Hz, 1H), 8.54–8.52 (m, 1H), 7.62–7.59 (m, 2H), 7.47 (dt, J = 1.8, 7.8 Hz, 1H), 7.20 (d, J = 2.1 Hz, 1H), 7.13–6.88 (m, 10H), 5.68 (d, J = 9.3 Hz, 1H), 2.37 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.4, 147.7, 142.7, 140.9, 140.1, 138.5, 138.3, 137.2, 133.4, 132.3, 131.2, 129.2, 127.9, 127.5, 126.9, 126.4, 125.9, 124.3, 122.4, 60.6, 21.3 ppm; HRMS (ESI): m/z calcd for $C_{25}H_{22}ClN_2O_2S$: 449.10850 $[M+H]^+$; found: 449.10879.

Compound 3fa: Obtained as a white solid by column chromatography (petroleum ether/ethyl acetate/CH_2Cl_2, 6:1:1 to 5:1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.13 (d, J = 9.6 Hz, 1H), 8.52–8.50 (m, 1H), 7.63 (d, J = 8.1 Hz, 2H), 7.43 (dt, J = 1.8, 7.8 Hz, 1H), 7.17–7.03 (m, 5H), 6.97–6.83 (m, 7H), 5.77 (d, J = 9.6 Hz, 1H), 2.78–2.68 (m, 1H), 2.31 (s, 3H), 1.16 (d, J = 3.3 Hz, 3H), 1.14 ppm (d, J = 3.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.9, 148.9, 147.3, 142.1, 140.8, 139.6, 139.0, 137.0, 136.9, 131.6, 129.7, 129.1, 127.2, 126.8, 126.0, 125.9, 125.5, 124.4, 121.7, 61.8, 33.4, 23.8, 23.4, 21.3 ppm; HRMS (ESI): m/z calcd for $C_{28}H_{29}N_2O_2S$: 457.19443 $[M+H]^+$; found: 457.19458.

Compound 3ga: Obtained as a white solid (easily melted by warming) by column chromatography (hexane/ethyl acetate, 3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.59–8.58 (m, 1H), 7.90 (d, J = 8.8 Hz, 1H), 7.64 (d, J = 8.4 Hz, 2H), 7.30–7.27 (m, 1H), 7.10–7.05 (m, 4H), 6.93–6.91 (m, 3H), 6.84–6.82 (m, 3H), 6.66 (t, J = 8.0 Hz, 2H), 5.54 (d, J = 9.2 Hz, 1H), 3.64 (s, 3H), 2.36 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.5, 155.8, 148.0, 142.4, 141.7, 140.7, 138.6, 135.4, 129.1, 129.0, 128.5, 127.4, 127.3, 127.0, 126.1, 125.7, 122.8, 121.8, 110.7, 60.9, 55.8, 21.4 ppm; HRMS (ESI): m/z calcd for $C_{26}H_{25}N_2O_3S$: 445.15804 $[M+H]^+$; found: 445.15797.

Compound 3ha: Obtained as a white solid by column chromatography (hexane/ethyl acetate, 5:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.74 (d, J = 9.3 Hz, 1H), 8.51–8.49 (m, 1H), 7.63–7.59 (m, 2H), 7.44 (dt, J = 1.8, 7.8 Hz, 1H), 7.09–7.04 (m, 3H), 7.02 (d, J = 7.8 Hz, 1H), 6.93–6.86 (m, 6H), 6.59 (d, J = 9.9 Hz, 1H), 5.58 (d, J = 9.6 Hz, 1H), 2.35 (s, 3H), 2.22 ppm (d, J = 1.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.4 (d, J = 246.6 Hz), 158.9, 147.5, 142.6, 140.1, 139.2 (d, J = 6.9 Hz), 138.6, 137.0, 135.0 (d, J = 3.5 Hz), 134.5 (d, J = 5.7 Hz), 129.1, 127.4, 127.0, 126.4, 126.0, 124.4, 123.9 (d, J = 17 Hz), 121.9, 117.7 (d, J = 23.1 Hz), 60.7, 21.3, 14.0 (d, J = 2.9 Hz) ppm; HRMS (ESI): m/z calcd for $C_{26}H_{24}FN_2O_2S$: 447.15370 $[M+H]^+$; found: 447.15489.

Compound 3oa: Obtained as a white solid (with some colorless slabby oil) by column chromatography (petroleum ether/ethyl acetate, 3:1 to 2:1 to 1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.58 (d, J = 9.2 Hz, 1H), 8.51 (d, J = 4.4 Hz, 1H), 7.60 (d, J = 8.0 Hz, 2H), 7.47 (dt, J = 0.8, 7.6 Hz, 1H), 7.23 (s, 1H), 7.10–7.03 (m, 5H), 6.95–6.91 (m, 6H), 5.71 (d, J = 9.2 Hz, 1H), 4.64 (s, 2H), 2.33 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.5, 147.3, 142.4, 140.6, 140.5, 139.3, 139.1, 138.7, 137.2, 131.1, 129.8, 129.1, 127.4, 126.9, 126.6, 126.3, 126.0, 124.5, 122.0, 64.4, 60.8, 21.4 ppm; HRMS (ESI): m/z calcd for $C_{26}H_{25}N_2O_3S$: 445.15804 $[M+H]^+$; found: 445.15899.

Compound 3pa: A mixture of two diastereoisomers was obtained as a white slabby solid by column chromatography (petroleum ether/ethyl acetate/CH_2Cl_2, 5:1:1 then petroleum ether/ethyl acetate, 3:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.79 (d, J = 9.6 Hz, 0.5H), 8.73 (d, J = 9.3 Hz, 0.5H), 8.51–8.49 (m, 1H), 7.59–7.55 (m, 2H), 7.43 (dt, J = 1.8, 7.8 Hz, 1H), 7.37–7.23 (m, 6H), 7.12–6.83 (m, 10H), 5.80–5.79 (m, 1H), 5.69 (d, J = 3.0 Hz, 0.5H), 5.66 (d, J = 3.0 Hz, 0.5H), 2.34 (br, 1H), 2.28 (s, 1.5H), 2.22 ppm (s, 1.5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.3, 159.3, 147.1, 143.5, 143.5, 143.4, 142.4, 140.4, 139.1, 139.0, 138.7, 137.5, 131.1, 131.0, 129.7, 129.3, 129.0, 128.6, 127.8, 127.8, 127.4, 126.9, 126.9, 126.6, 126.6, 126.6, 126.3, 126.3, 126.1, 124.7, 124.7, 122.2, 75.7, 75.66, 60.8, 60.8, 21.4, 21.3 ppm; HRMS (ESI): m/z calcd for $C_{32}H_{29}N_2O_3S$: 521.18934 $[M+H]^+$; found: 521.18984.

Compound 3qa: A mixture of two diastereoisomers was obtained as a white solid by column chromatography (petroleum ether/ethyl acetate/CH_2Cl_2, 5:1:1 then petroleum ether/ethyl acetate, 3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.79–8.74 (m, 1H), 8.49–8.46 (m, 1H), 7.57 (d, J = 8.0 Hz, 2H), 7.43–7.23 (m, 7H), 7.11–6.83 (m, 11H), 5.69 (d, J = 4.0 Hz, 0.5H), 5.67 (d, J = 4 Hz, 0.5H), 2.44 (br, 1H), 2.28–2.27 (m, 3H), 1.89 (s, 1.5H), 1.88 ppm (s, 1.5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.8, 159.8, 147.6, 147.5, 147.4, 147.4, 142.2, 142.2, 140.6, 140.6, 139.2, 139.1, 138.7, 138.3, 136.9, 136.9, 130.8, 130.7, 129.0, 128.7, 128.2, 127.3, 127.1, 126.9, 126.9, 126.2, 126.0, 125.7, 125.6, 125.3, 124.5, 124.5, 121.9, 121.9, 75.8, 60.9, 60.9, 31.0, 30.8, 21.4, 21.3 ppm; HRMS (ESI): m/z calcd for $C_{33}H_{31}N_2O_3S$: 535.20499 $[M+H]^+$; found: 535.20495.

Compound 3qa′: Obtained as white solid by column chromatography (petroleum ether/ethyl acetate/CH_2Cl_2, 5:1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.82 (d, J = 9.6 Hz, 1H), 8.52–8.51 (m, 1H), 7.64 (d, J = 8.0 Hz, 2H), 7.41 (dt, J = 1.6, 7.6 Hz, 1H), 7.38–7.29 (m, 5H), 7.18 (d, J = 2.0 Hz, 1H), 7.09–7.03 (m, 4H), 7.00–6.92 (m, 6H), 6.87 (d, J = 8.0 Hz, 1H), 5.73 (d, J = 9.6 Hz, 1H), 5.47 (d, J = 0.8 Hz, 1H), 5.44–5.43 (m, 1H), 2.33 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.8, 149.2, 147.6, 142.3, 141.0, 140.9, 140.6, 139.3, 139.3, 139.0, 137.0, 131.1, 131.1, 129.1, 128.3, 128.1, 127.9, 127.9, 127.4, 127.0, 126.3, 126.0, 124.5, 121.9, 114.8, 61.2, 21.4 ppm; HRMS (ESI): m/z calcd for $C_{33}H_{29}N_2O_2S$: 517.19443 $[M+H]^+$; found: 517.19420.

Compound 3bc: Obtained as white solid by column chromatography (petroleum ether/ethyl acetate/CH_2Cl_2, 5:1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.67 (d, J = 9.6 Hz, 1H), 8.55–8.53 (m, 1H), 7.60 (d, J = 8.4 Hz, 2H), 7.45 (dt, J = 1.8, 7.8 Hz, 1H), 7.28–7.18 (m, 2H), 7.12–6.99 (m, 5H), 6.88 (d, J = 8.1 Hz, 1H), 6.80 (t, J = 7.5 Hz, 1H), 6.72–6.64 (m, 3H), 5.67 (d, J = 9.3 Hz, 1H), 2.33 (s, 3H), 2.05 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.0, 147.5, 142.3, 140.5, 140.0, 139.6, 138.8, 136.8, 136.8, 131.3, 130.9, 129.0, 128.1, 127.6, 127.3, 126.9, 126.9, 126.7, 124.5, 123.3, 121.8, 61.3, 21.4, 21.1 ppm; HRMS (ESI): m/z calcd for $C_{26}H_{25}N_2O_2S$: 429.16313 $[M+H]^+$; found: 429.16305.

Compound 3be: Obtained as white slabby oil by column chromatography (petroleum ether/ethyl acetate/CH_2Cl_2, 5:1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.93 (d, J = 9.6 Hz, 1H), 8.53 (dd, J = 0.9, 4.8 Hz, 1H), 7.62 (d, J = 8.4 Hz, 2H), 7.46 (dt, J = 1.8, 7.8 Hz, 1H), 7.33–7.00 (m, 11H), 6.89 (d, J = 7.8 Hz, 1H), 5.72 (d, J = 9.3 Hz, 1H), 2.34 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.4, 147.4, 145.0, 142.5, 139.2, 139.0, 138.5, 137.1, 131.4, 131.2, 129.1 (2C), 128.3, 128.3 (q, J = 32.0 Hz), 128.0, 126.8 (2C), 126.3 (2C), 124.4, 124.1 (q, J = 3.6 Hz, 2C), 123.9 (q, J =

270.0 Hz), 122.1, 61.2, 21.3 ppm; HRMS (ESI): *m/z* calcd for $C_{26}H_{22}FN_2O_2S$: 483.13486 $[M+H]^+$; found: 483.13370.

Compound 3bf: Obtained as a yellow solid by column chromatography (petroleum ether/ethyl acetate/CH_2Cl_2, 6:1:1 to 5:1:1). ^1H NMR (300 MHz, $CDCl_3$): $\delta=9.13$ (d, $J=9.6$ Hz, 1H), 8.53–8.51 (m, 1H), 7.81–7.76 (m, 2H), 7.62–7.59 (m, 2H), 7.48 (dt, $J=1.8$, 7.8 Hz, 1H), 7.34–7.24 (m, 2H), 7.19–7.06 (m, 6H), 7.01–6.98 (m, 1H), 6.96 (d, $J=8.1$ Hz, 1H), 5.73 (d, $J=9.3$ Hz, 1H), 2.34 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=159.2$, 148.6, 147.4, 146.2, 142.7, 139.0, 138.4, 138.3, 137.4, 131.6, 131.3, 129.2, 128.5, 128.3, 126.8, 126.8, 124.4, 122.4, 122.3, 61.3, 21.3 ppm; HRMS (ESI): *m/z* calcd for $C_{25}H_{22}N_3O_4S$: 460.13255 $[M+H]^+$; found: 460.13291.

Compound 3bl: Obtained as a white solid by column chromatography (petroleum ether/ethyl acetate/CH_2Cl_2, 5:1:1). ^1H NMR (300 MHz, $CDCl_3$): $\delta=8.70$ (d, $J=9.3$ Hz, 1H), 8.54–8.52 (m, 1H), 7.60 (d, $J=8.4$ Hz, 2H), 7.48 (dt, $J=1.8$, 7.8 Hz, 1H), 7.28–7.19 (m, 2H), 7.12–6.99 (m, 5H), 6.93 (d, $J=8.1$ Hz, 1H), 6.84 (d, $J=8.4$ Hz, 2H), 6.48–6.45 (m, 2H), 5.65 (d, $J=9.3$ Hz, 1H), 3.64 (s, 3H), 2.33 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=159.9$, 157.9, 147.5, 142.3, 139.9, 139.5, 138.7, 137.0, 132.9, 131.4, 130.8, 129.0 (2C), 128.1, 127.6, 127.2 (2C), 126.9 (2C), 124.4, 121.9, 112.8 (2C), 60.9, 55.1, 21.4 ppm; HRMS (ESI): *m/z* calcd for $C_{26}H_{25}N_2O_3S$: 445.1580 $[M+H]^+$; found: 445.1579.

Compound 3bm: Obtained as a white solid by column chromatography (petroleum ether/ethyl acetate/CH_2Cl_2, 5:1:1). ^1H NMR (300 MHz, $CDCl_3$): $\delta=8.90$ (d, $J=9.3$ Hz, 1H), 8.55–8.53 (m, 1H), 7.65–7.59 (m, 3H), 7.50–7.19 (m, 8H), 7.14–7.03 (m, 6H), 6.82 (d, $J=7.8$ Hz, 1H), 5.85 (d, $J=9.3$ Hz, 1H), 2.33 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=$ 159.8, 147.5, 142.4, 139.7, 139.6, 138.8, 137.9, 136.8, 132.6, 131.9, 131.4, 131.1, 129.1, 128.3, 127.7, 127.2, 127.1, 127.0, 125.7, 125.4, 124.8, 124.6, 124.3, 121.9, 61.5, 21.3 ppm; HRMS (ESI): *m/z* calcd for $C_{29}H_{25}N_2O_2S$: 465.16313 $[M+H]^+$; found: 465.16340.

Compound 3bn: Obtained as a white solid by column chromatography (petroleum ether/ethyl acetate/CH_2Cl_2, 5:1:1). ^1H NMR (300 MHz, $CDCl_3$): $\delta=8.81$ (d, $J=9.6$ Hz, 1H), 8.56–8.54 (m, 1H), 7.63 (d, $J=8.1$ Hz, 2H), 7.45–7.34 (m, 5H), 7.30–7.21 (m, 3H), 7.17–6.98 (m, 9H), 6.91–6.89 (m,1H), 5.74 (d, $J=9.6$ Hz, 1H), 2.34 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=159.8$, 147.5, 142.3, 140.7, 139.9, 139.8, 139.5, 138.9, 138.7, 136.9, 131.4, 131.0, 129.1, 128.6, 128.2, 127.7, 127.1, 126.9, 126.8, 126.4, 126.0, 124.5, 121.9, 61.2, 21.4 ppm; HRMS (ESI): *m/z* calcd for $C_{31}H_{27}N_2O_2S$: 491.17878 $[M+H]^+$; found: 491.17860.

Compound 3bo: Obtained as a white solid (the solution in $CDCl_3$ was slightly blue) by column chromatography (petroleum ether/ethyl acetate/CH_2Cl_2, 6:1:1). ^1H NMR (300 MHz, $CDCl_3$): $\delta=8.61$ (d, $J=9.6$ Hz, 1H), 8.58–8.56 (m, 1H), 7.63–7.58 (m, 3H), 7.32–7.10 (m, 5H), 7.06 (d, $J=7.8$ Hz, 3H), 6.95–6.94 (m, 1H), 5.90 (q, $J=1.8$ Hz, 1H), 5.74–5.73 (m, 1H), 5.67 (d, $J=9.3$ Hz, 1H), 2.33 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=159.8$, 153.1, 147.6, 142.5, 141.3, 139.7, 138.6, 137.5, 137.1, 131.1, 130.6, 129.1, 128.4, 128.1, 127.0, 124.1, 122.1, 109.9, 106.9, 56.9, 21.4 ppm; HRMS (ESI): *m/z* calcd for $C_{23}H_{21}N_2O_3S$: 405.12674 $[M+H]^+$; found: 405.12674.

Compound 3ra: Obtained as a white solid by column chromatography (hexane/ethyl acetate, 5:1). ^1H NMR (400 MHz, $CDCl_3$): $\delta=7.80$ (d, $J=9.6$ Hz, 1H), 7.63 (d, $J=8.4$ Hz, 2H), 7.58 (d, $J=1.6$ Hz, 1H), 7.30–7.27 (m, 1H), 7.17–7.12 (m, 2H), 7.09 (t, $J=8.4$ Hz, 3H), 7.03–7.01 (m, 3H), 6.99 (d, $J=2.4$ Hz, 1H), 6.92–6.90 (m, 2H), 6.08 (t, $J=2.0$ Hz, 1H), 5.69 (d, $J=1.6$ Hz, 1H), 2.33 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=$ 142.6, 140.3, 139.5, 138.8, 138.4, 136.9, 131.5, 130.9, 129.2, 128.5, 128.3, 127.7, 127.0, 126.7, 125.5, 106.8, 59.6, 21.4 ppm; HRMS (ESI): *m/z* calcd for $C_{23}H_{22}N_3O_2S$: 404.14272 $[M+H]^+$ and $C_{23}H_{21}KN_3O_2S$: 442.09861 $[M+K]^+$; found: 404.14278 and 442.09893.

***N*-{(4-Formylphenyl)[2-(pyridin-2-yl)phenyl]methyl}-4-methylbenzenesulfonamide (10)**: The reaction was carried out following the standard procedure. Catalyst $[Cp^*Rh(CH_3CN)_3][SbF_6]_2$ (4.2 mg, 0.005 mmol) and substrate **9** (15.0 mg, 0.034 mmol) were added into a pre-dried Schlenk tube under air atmosphere. The reaction tube was then evacuated and refilled with N_2. After the addition of freshly distilled *t*BuOH (0.5 mL) and toluene (0.5 mL) by using a syringe, the reaction mixture was stirred in the sealed tube at 90 °C under N_2 atmosphere in a Wattecs Parallel Reactor for 24 h. Because the product **10** was difficult to isolate in pure form from $TsNH_2$, the yield was determined NMR spectroscopic analysis. Upon completion of the reaction, the solvent was evaporated by rotary evaporator, after which (methoxymethyl)benzene (4.0 mg, 0.03274 mmol) was added as internal standard to determine the yield of the desired product **10**. After dissolving the residue in $CDCl_3$, the mixture was detected by 400 MHz ^1H NMR spectroscopic analysis. Comparison of the ^1H NMR data of this system and the data of **10** identified the characterization peak and provided the NMR yield. The characteristic peaks are as follows. ^1H NMR (400 MHz, $CDCl_3$): $\delta=9.80$ (s, 0.31H, CHO), 5.72 (d, $J=7.6$ Hz, 0.35H, benzyl CH of product), 4.46 (s, 2H, CH_2 of internal standard), 3.39 ppm (s, 3H, CH_3 of internal standard). The ^1H NMR yield was 34%. The characterization data of pure compound **10** obtained by preparative TLC was as follows: ^1H NMR (400 MHz, $CDCl_3$): $\delta=9.80$ (s, 1H), 9.07 (d, $J=9.2$ Hz, 1H), 8.52 (d, $J=4.4$ Hz, 1H), 7.62 (d, $J=8.0$ Hz, 2H), 7.46–7.42 (m, 3H), 7.31–7.23 (m, 2H), 7.16 (d, $J=8.0$ Hz, 2H), 7.12–7.06 (m, 4H), 7.00 (d, $J=7.6$ Hz, 1H), 6.90 (d, $J=8.0$ Hz, 1H), 5.72 (d, $J=9.2$ Hz, 1H), 2.34 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=191.8$, 159.5, 148.1, 147.5, 142.6, 139.2, 138.9, 138.6, 137.2, 134.5, 131.6, 131.4, 129.2, 128.8, 128.4, 128.1, 126.8, 126.6, 124.4, 122.2, 61.6, 21.4 ppm; HRMS (ESI): *m/z* calcd for $C_{26}H_{23}N_2O_3S$: 443.14239 $[M+H]^+$; found: 443.14301.

Competition experiment: The competition reaction was conducted with 2-phenylpyridine **5** and alcohol **1a** with imine **2a**. Catalyst $[Cp^*Rh(CH_3CN)_3][SbF_6]_2$ (8.3 mg, 0.01 mmol), alcohol **1a** (55.1 mg, 0.20 mmol), and aldimine **2a** (155.6 mg, 0.60 mmol) were added into a pre-dried Schlenk tube under air atmosphere. The reaction tube was degassed three times and the tube was filled with N_2, then 2-phenylpyridine **5** (28.6 μL, 0.2 mmol) and freshly distilled *t*BuOH (1.0 mL) were added by microinjector and syringe, respectively. The reaction mixture was stirred in the sealed tube at 90 °C under N_2 atmosphere in a Wattecs Parallel Reactor for 3 h. After cooling to RT, the solvent was removed in vacuo and the yield was determined by NMR spectroscopic analysis. After evaporation of the solvent, (methoxymethyl)benzene (5 μL, 0.1154 mmol) was added as internal standard. ^1H NMR (400 MHz, $CDCl_3$): $\delta=4.46$ (s, 2.00H, CH_2 of (methoxymethyl)benzene), 5.71 (d, $J=5.6$ Hz, 1.60H, CH of **3ba**), 5.66 ppm (s, 1.81H, CH of **3aa**). The NMR yield of **3aa** and **3ba** were 35 and 31%, respectively.

Deuterium Labeling Experiment: Catalyst $[Cp^*Rh(CH_3CN)_3][SbF_6]_2$ (4.2 mg, 0.005 mmol), 1-phenyl-[3,4,5,6–4D-2-(pyridine-2-yl)]benzyl alcohol **7** (26.5 mg, 0.10 mmol) and aldimine **2a** (77.80 mg, 0.30 mmol) were added into a pre-dried Schlenk tube under air atmosphere. The reaction tube was then evacuated and refilled with N_2. After the addition of freshly distilled *t*BuOH (1.0 mL) by using a syringe, the reaction mixture was stirred in the sealed tube at 90 °C under N_2 atmosphere in a Wattecs Parallel Reactor for 3 h. After cooling to RT, the solvent was removed in vacuo and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc/CH_2Cl_2, 5:1:1) to afford compound **8** as a white solid (80%, 33.4 mg). ^1H NMR (300 MHz, $CDCl_3$): $\delta=8.79$ (d, $J=9.6$ Hz, 1H), 8.54–8.52 (m, 0.95H), 7.62–7.59 (m, 2H), 7.47 (dt, $J=1.8$, 7.8 Hz, 1H), 7.21 (s, 1H), 7.12–7.03 (m, 3H), 7.00–6.86 (m, 6H), 5.71 (d, $J=9.6$ Hz, 1H), 2.33 ppm (s, 3H). From this result, it can be concluded that the H/D ratio of the product is approximately 95:5.

In situ NMR detection (Figure 1): This experiment was conducted in a Young NMR tube on 0.025 mmol scale in 405 μL solvent (0.06173 M), which has lower concentration than in our standard reaction conditions. This was because larger amounts of substrate did not dissolve well in the NMR tube at RT, which affected the locking and shimming. Solutions were prepared that contained **1b** (65.33 mg, 0.25 mmol) and catalyst (41.64 mg, 0.05 mmol) dissolved in freshly distilled $[D_8]$toluene (1 mL, 0.025 mmol/100 μL) and distilled acetone (10 mL, 0.00125 mmol/250 μL) in a volumetric flask. In addition (methoxymethyl)benzene (229.1 mg, 1.875 mmol) was dissolved in mesitylene (5 mL) as internal standard solution (0.001875 mmol/5 μL). To a pre-dried NMR tube, catalyst solution (250 μL, 0.00125 mmol) was added by using a microinjector, and then the solvent was removed under vacuum. Then $[D_8]$toluene (100 μL) was then added and vigorous shaking and slight heating were applied to dissolve the catalyst. Imine **2a** (19.6 mg, 0.075 mmol) was added to the NMR

tube, followed by further [D_8]toluene (150 μL) to dissolve the imine. Internal standard solution (5 μL, 0.001875 mmol, 7.5%), alcohol **1b** solution (100 μL, 0.025 mmol), and [D_8]toluene (50 μL) were then added sequentially. Finally, the NMR tube was filled with N_2 and sealed. The sample was first tested at RT to ensure that locking, shimming were satisfactory, then the sample was heated to 90°C before the data were collected (the experiment was conducted with a Bruker 500 M NMR spectrometer). For the first hour, data were collected every 5 min, and subsequently, data were collected every 10 min. ^{1}H NMR data were selected as concentration detection signals. The following characteristic peaks were used to determine the concentration of the arious species: ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 9.70$ (s, CHO of benzaldehyde), 8.54 (d, 2-phenyl pyridine), 6.02 (s, CH of product), 5.94 (s, CH of alcohol **1b**), 4.26 (s, CH_2 of internal standard), 3.17 (s, CH_3 of internal standard).

Transformation between alcohols: Typical procedure for 12 (Table 4): A 50 mL Schlenk tube was heated using a heat gun under vacuum to dry the tube. After cooling to RT, catalyst [Cp*Rh(CH_3CN)$_3$][SbF_6]$_2$ (8.3 mg, 0.01 mmol), alcohol **1b** (0.2 mmol), and benzaldehyde derivative **11** (0.60 mmol) were added in sequence to the tube under air atmosphere. The reaction tube was then evacuated and refilled with N_2. After the addition of freshly distilled *t*BuOH (1.0 mL, condition A) or CH_2Cl_2 (1.0 mL, condition B), the reaction mixture was stirred in the sealed tube at 90°C under N_2 atmosphere in a Wattecs Parallel Reactor for the time indicated. After cooling to RT, the solvent was removed in vacuo and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc, 6:1 to 2:1, or petroleum ether/EtOAc/CH_2Cl_2, 6:1:1 to 3:1:1) to afford compound **12** as a white solid.

Compound 12a: Obtained by column chromatography (petroleum ether/EtOAc/CH_2Cl_2, 4:1:1) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta =$ 8.55–8.54 (m, 1H), 8.02–8.00 (m, 2H), 7.72 (dt, $J = 1.6$, 8.0 Hz, 1H), 7.51–7.40 (m, 7H), 7.25–7.23 (m, 2H), 5.85 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 159.30$, 151.21, 147.51, 146.65, 142.43, 139.64, 137.78, 131.13, 130.42, 129.33, 128.45, 127.05, 124.16, 122.78, 122.46, 74.58 ppm; HRMS (ESI): *m*/*z* calcd for $C_{18}H_{15}N_2O_3$: 307.10772 $[M+H]^+$; found: 307.10801.

Transformation from allylic alcohol into allylic amine: Typical procedure for 14 (Table 5): A 50 mL Schlenk tube was heated using a heat gun under vacuum to dry the tube. After cooling to RT, catalyst [Cp*Rh(CH_3CN)$_3$][SbF_6]$_2$ (8.3 mg, 0.01 mmol), alcohol **13** (0.2 mmol), and aldimine derivative **2** (0.60 mmol) were added in sequence to the tube under air atmosphere. The reaction tube was then evacuated and refilled with N_2. After the addition of freshly distilled *t*BuOH (1.0 mL), the reaction mixture was stirred in the sealed tube at 90 or 110°C under N_2 atmosphere in a Wattecs Parallel Reactor for the time indicated. After cooling to RT, the solvent was removed in vacuo and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc, 6:1 to 2:1, or petroleum ether/EtOAc/CH_2Cl_2, 6:1:1 to 3:1:1) to afford compound **14** as a white solid.

Compound 14b: Obtained by column chromatography (petroleum ether/EtOAc/CH_2Cl_2, 5:1:1) as a light-yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 9.20$–9.17 (br, 1H), 8.54 (d, $J = 4.0$ Hz, 1H), 7.67 (dt, $J = 1.2$, 7.6 Hz, 1H), 7.49 (d, $J = 8.0$ Hz, 2H), 7.16–7.01 (m, 7H), 6.86–6.82 (m, 1H), 5.56 (s, 1H), 2.74–2.69 (m, 1H), 2.54–3.48 (m, 2H), 2.36 (s, 3H), 2.30–2.22 (m, 1H), 1.77–1.73(m, 1H), 1.62–1.57 ppm (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 162.7$ (d, $J = 240.0$ Hz), 154.1, 148.0, 142.8 (d, $J =$ 71.0 Hz), 142.5, 138.3, 137.1, 135.8, 129.6 (d, $J = 100.0$ Hz), 129.0, 126.9, 122.7 (d, $J = 3.0$ Hz), 122.6, 121.77, 114.0 (d, $J = 20.0$ Hz), 56.2, 39.2, 36.5, 21.4, 21.4 ppm; HRMS: *m*/*z* calcd for $C_{24}H_{24}FN_2O_2S$: 423.15370 $[M+H]^+$; found: 423.15386.

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