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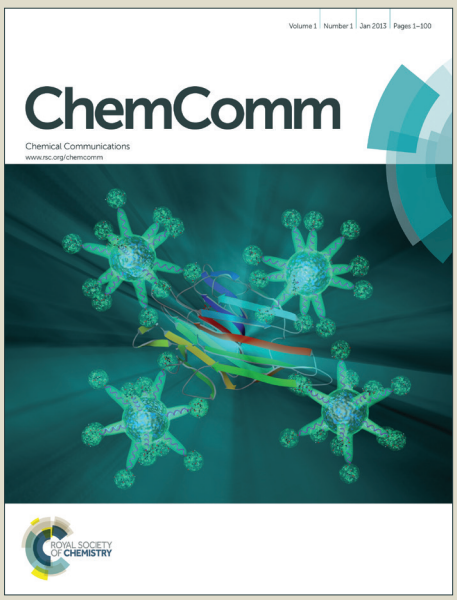

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Rh(III)-catalyzed and alcohol-involved carbenoid C–H insertion of *N*-phenoxyacetamides by α-diazomalonates

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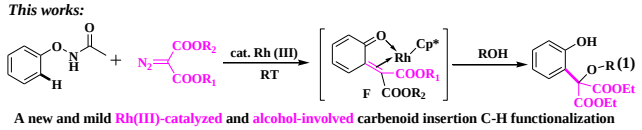
Here we report a new and mild Rh(III)-catalyzed and alcohol-involved carbenoid C–H insertion of *N*-phenoxyacetamides by α-diazomalonates. This reaction provided a straightforward way for installing both α-quaternary carbon center and free-OH moiety into the phenyl rings, thus giving access to privileged 2-(2-hydroxyphenyl)-2-alkoxymalonates with good substrate/functional group tolerance.

Transition-metal-catalyzed functionalization of inert C–H bonds has emerged as one of the most popular and powerful tools for step- and atom-economical construction of diversified complex molecules, and to date, significant progress has been made in this hot area of research.[1] In general, to achieve the efficient C–H functionalization, the use of a combination of directing groups (DGs) and stoichiometric or excess amounts of external oxidants is commonly required. Indeed, they could improve the regioselectivity as well as reaction efficiency of the C–H activation reactions. However, in spite of the success, this strategy also presents two main disadvantages: (1) the introduction of DGs often leaves a chemical trace in the products, limiting their structural diversity; (2) the compulsive use of external oxidants involves relatively harsh reaction conditions and produces stoichiometric amounts of related metal wastes.

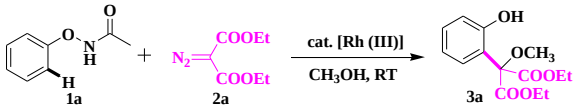
To address aforementioned drawbacks, recently one emerging strategy to develop an innovative oxidizing-directing group (ODG) which acts simultaneously as both DG and internal oxidant has attracted much attention.[2] As a consequence, remarkable advances has been made and several versatile ODGs such as N–OR,[3] N–NR[4] and O–NHAc[5] are stood out.

On the other hand, recently diazo compounds have been widely used as powerful cross-coupling partners for transition-metal-catalyzed direct C–H functionalization, of which Rh catalysts plays a particularly prominent role.[6,7] For example, inspired by the pioneering work of Yu,[7a] afterwards the groups of Rovis,[3k] Glorius,[7b] Li,[7c,d] Cui,[3l,7e] Yu,[7f] Wang,[7g,h] Chang,[7i] Zhou,[7j] Cramer,[7k] Liu[7l] and our groups[7m,n] have displayed the successful exploration of diazo compounds as the cross-coupling partners in Rh(III)-catalyzed C–H functionalization with a DG-assisted strategy.



Taking advantage of above information and in continuation of our interest in the Rh(III)-catalyzed C–H functionalization, we herein describe a new and mild Rh(III)-catalyzed carbenoid C–H insertion (*ortho*-alkylation) of diverse *N*-phenoxyacetamides by α-diazomalonates for direct synthesis of 2-(2-hydroxyphenyl)-2-alkoxymalonates, in which O–NHAc group was used as the ODG ((eqn (1)). Notably, in this reaction, alcohol also employed as the reagents to mediate the alcoholysis of intermediate **F** *via* a similar 1,4-addition pathway, thereby installing both α-quaternary carbon center and free-OH moiety into the phenyl ring, which was very different from the reported reactions of Rh(III)-catalyzed carbenoid insertion.[3k,l,7]

Table 1 Optimization Studies[a]



Entry	Catalyst system (mol %)	Solvent (mL)	Yield[b] (%)
1	$[Cp^*Rh^{III}(MeCN)_3](SbF_6)_2$ (5)	CH_3OH (1.0)	83
2	**$[Cp^*Rh^{III}(MeCN)_3](SbF_6)_2$ (2.5)**	**CH_3OH (1.0)**	**81**
3	$[Cp^*Rh^{III}(MeCN)_3](SbF_6)_2$ (1)	CH_3OH (1.0)	45
4	$[Cp^*Rh^{III}(MeCN)_3](SbF_6)_2$ (2.5)	CH_3OH (0.5)	70
5	$[Cp^*Rh^{III}(MeCN)_3](SbF_6)_2$ (0)	CH_3OH (1.0)	0
6	$[Cp^*RhCl_2]_2$ (2.5)/$AgSbF_6$ (100)	CH_3OH (1.0)	58
7	$[Cp^*Rh(OAc)_2]_2$	CH_3OH (1.0)	0
8[c]	$[Cp^*Rh^{III}(MeCN)_3](SbF_6)_2$ (2.5)	CH_3OH (1.0)	78

[a]Reaction conditions: **1a** (0.10 mmol, 1.0 equiv), **2a** (0.12 mmol, 1.2 equiv), Rh catalyst (X mol%), solvent (0.5 or 1.0 mL), 10 h, under air. [b]Isolated yields. [c] Performed on a 2.0 mmol scale.

Given the successful history of $[Cp^*Rh(MeCN)_3](SbF_6)_2$ in the field of C–H activation,[8] therefore, at the outset of this study, we chose it as the Rh(III) catalyst for the reaction development with *N*-phenoxyacetamide **1a** as the model substrate and MeOH as the solvent (Table 1). To our surprise, a preliminary survey of diazo compounds[9] showed that the reaction of **1a** with diethyl 2-diazomalonate **2a** at room temperature for 10 h proceeded successfully to deliver the free-OH-substituted alkylation product **3a** in 83% yield (entry 1), in which O–NHAc group was used as the ODG[5] and MeOH was used not only as the solvent but also as the reagent in the catalytic reaction, thereby leading to installing a α-quaternary carbon center into the *ortho*-position of hydroxy group. Encouraged by this finding, we next investigated the effects of catalyst loading and concentration for this reaction optimization. Reducing the loading of catalyst from 5 mol% to 2.5 mol% resulted in the isolation of **3a** in 81% yield (entry 2). However, further reducing the loading of catalyst to 1 mol% led to a significant decrease in the product yield (45% yield, entry 3). Similarly, decreasing the amount of MeOH also gave lower conversion (entry 4). As predicted, no desired product was

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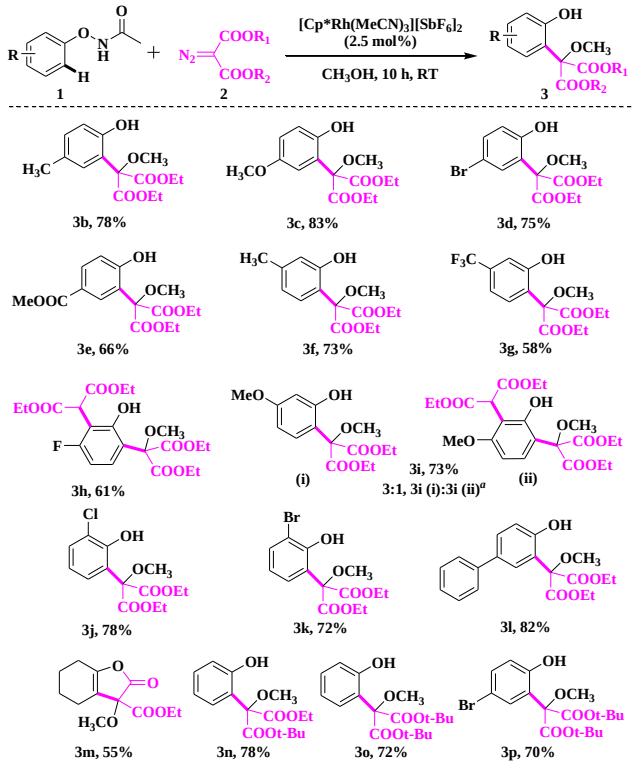
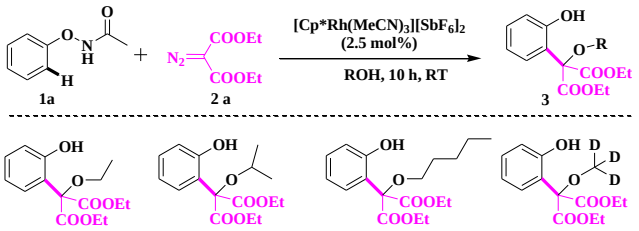
formed in the absence of catalyst (entry 5). Finally, change of catalyst $[Cp^*Rh(MeCN)_3](SbF_6)_2$ to other well-known Rh(III) catalysts such as $[Cp^*RhCl_2]_2$ and $[Cp^*Rh(OAc)_2]_2$ inhibited the process (entries 6-7). In summary, the optimal conditions were identified as the following: 2.5 mol% $[Cp^*Rh(MeCN)_3](SbF_6)_2$ in 1.0 mL of MeOH at room temperature for 10 h under an atmosphere of air. Finally, the reaction could be performed on a 2.0 mmol scale under the optimized conditions with decent isolated yield (78%, entry 8).



Scheme 1 Scope of *N*-phenoxyacetamides. Reaction conditions: **1** (0.10 mmol) and **2** (0.12 mmol) in MeOH (1.0 mL) at room temperature for 10 h under air. Isolated yields. [a]The ratio was determined by isolated yields.

With this efficient catalytic system established, we sought to explore the scope of substrates and generality of this reaction. As shown in Scheme 1, diazomalonate **2a** efficiently coupled with a variety of substituted *N*-phenoxyacetamides in MeOH to provide the corresponding 2-(2-hydroxyphenyl)-2-alkoxymalonates in moderate to good yields. Substitutions at the *para*- (**3b-e** and **3l**), *meta*- (**3f-i**), or *ortho*- (**3j-k**) postion were all well tolerated. Importantly, the reaction also showed good compatibility with a wide range of valuable functional groups such as methyl, methoxy, bromo chloro, fluoro, ester, and trifluoromethyl substituents. Tolerance to the chloro (**3j**), bromo (**3d**, **3k** and **3p**), and ester (**3e**) functional groups was especially noteworthy since they could be used as versatile building-blocks for further synthetic transformations. The electronic nature of the substituents on the benzene ring of substrates **1** had no obvious influence on the reaction outcome, and in the present cases, *N*-phenoxyacetamides bearing both electron-donating and -withdrawing groups showed excellent reaction efficiency. Interestingly, substrates **1f** and **1g** bearing methyl and terfluoromethyl groups at *meta*-position, respectively, provided the corresponding products in moderate yields with exclusive regioselectivity. However, *meta*-fluoro-substituted derivative **1h** afforded the dialkylated product in 61% yield, where an additional substituent (1,3-diethoxy-1,3-dioxopropan-2-yl) was attached at the less-hindered site. Conjunctively, *meta*-methoxyl-substituted *N*-phenoxyacetamide **1i** gave a 3:1 mixture of products **3i (i)** and **3i (ii)**. Taken together, these results revealed that the type of the substituent at the *meta*-position played a key role in determining the reaction process. Moreover, polyaromatic diphenyl substrate could be accommodated in the catalytic system, giving the desired product **3l** in reasonably good yield (82%). Notably, the alkylation reaction with **2a** also tolerated the alkenyl substrate, which produced the interesting furanone **3n** in 55% yield with a stereogenic α-carbon center. In addition, *tert*-butyl diazomalonates **2b-c** was also investigated in the Rh(III) system. As shown in Scheme 1, **2b-c** coupled efficiently with *N*-phenoxyacetamides to offer the corresponding *ortho*-alkylation product **3n-p** in synthetically useful yields (78% for **3n**, 72% for **3o** and 70% for **3p**), where *tert*-butyl moiety was retained perfectly. The results further illustrated the remarkable robustness of our developed Rh(III) catalysis.



Scheme 2 Scope of alcohols. Reaction conditions: **1** (0.10 mmol) and **2** (0.12 mmol) in the corresponding alcohol (1.0 mL) at room temperature for 10 h under air. Isolated yields. [a]These reactions ran at 80 °C.

Since methanol has played dual roles as both reactant and reaction medium in this reaction (as shown above), subsequently several alkyl alcohols were evaluated in the current catalytic system (Scheme 2). As expected, the reactions occurred successfully under air to give the corresponding *ortho*-alkylated products **3q-3s** in 64%, 51% and 57% yields, respectively. Of note, the reaction also worked well in CD_3OD to afford the methyl-deuterated **3t** in good isolated yield (76%), which provided hints of the reaction mechanism.

Inspired by the above results and to obtain better insight into the reaction mechanism, a set of additional experiments were carried out (Scheme 3). First, **1a** was treated with $[Cp^*Rh(MeCN)_3](SbF_6)_2$ in CD_3OD (Scheme 3a) in the absence of diazomalonates. After stirring at room temperature for 3 h, 98% of **1a** was recovered and no deuterium incorporation was observed, revealing that the C–H bond activation step was largely irreversible. Next, the isotope-labeling experiment was conducted with a deuterium-labeled *N*-phenoxyacetamide $[D_5]$-**1a**. As demonstrated in Scheme 3b, treatment of **2a** with the same amounts of both **1a** and $[D_5]$-**1a** for 30 min under standard conditions gave a relatively large KIE value (k_H/k_D = 2.7). The result suggested that C–H bond-cleavage process might be involved in the rate-limiting step. Subsequently, the competition experiment of equimolar amounts of **1f** and **1g** under the standrad reaction conditions with **2a** was carried out to to delineate the action mode of the reaction (Scheme 3c). The ratio of products showed that electron-deficient **1g** was preferentially converted (**3f**/**3g** = 1:10), revealing that the C-H activation might be *via* a concerted-metallation-deprotonation (CMD) mechanism.[3k,10] Moreover, *N*-methyl-substituted phenoxyacetamide **1o** was prepared and was designated as a substrate to evaluate the role of N–H bond (Scheme 3d). As expected, the reaction of **1o** and **2a** did not proceed, indicating that the N–H bond of O–NHAc was indispensable for this transformation, which is consistent with

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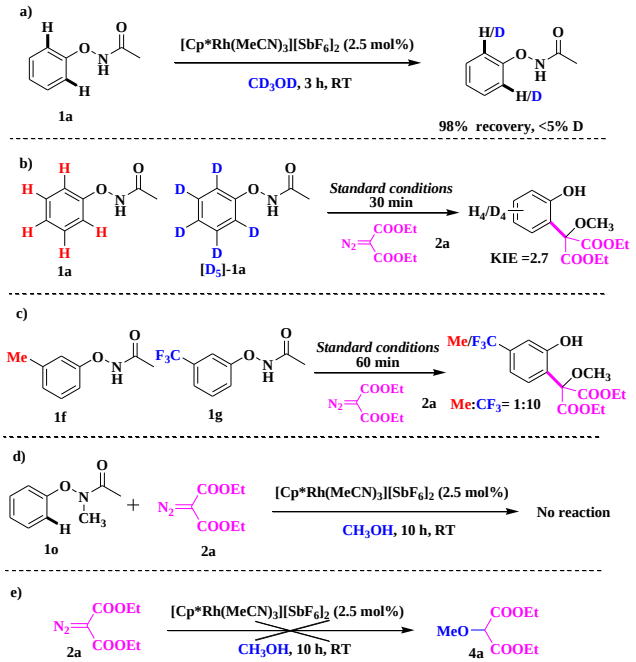
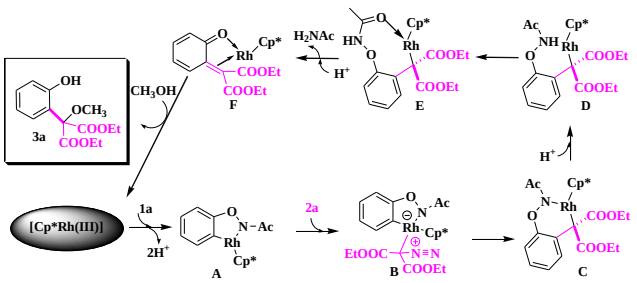
previous report by Lu and co-workers.[5b] Finally, an experiment using **2a** as the sole substrate in MeOH was performed under otherwise identical conditions. As demonstrated in Scheme 3e, the diethyl 2-methoxymalonate **4a** was not detected, providing clear evidence that MeOH was not involved in the classic metal-carbene insertion into C(sp^3)–H bond mechanism.[11]



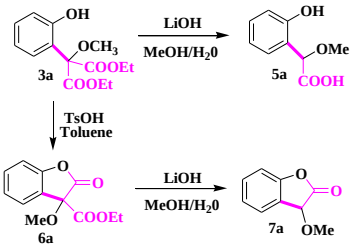
Scheme 3 Mechanistic experiments.

Taking the above observations and the mechanism studies of precedent literature into consideration, a plausible reaction mechanism is proposed in Scheme 4. First, the coordination of *N*-phenoxyacetamide **1a** to a [Cp*Rh(III)] species was the key rate-determining step for the regioselective C–H bond cleavage to form a five-membered rhodacyclic intermediate **A**. Further coordination of **A** with **2a** afforded the diazonium intermediate **B**. Subsequently, Rh(III)–carbene migratory insertion from **B** provided six-membered rhodacycle intermediate **C** with the emission of N_2. Protonolysis of **C** delivered the intermediate **D** *via* the Rh–N bond cleavage. Subsequently, the intramolecular coordination of intermediate **D** was occured to form intermediate **E**, followed by α-H elimination/intramolecular rearrangement to afford intermediate **F** with extrusion of acetamide. Finally, intermediate **F** underwent a similar 1,4-addition step by using MeOH as reactant to give the desired product **3a** along with the regeneration of the rhodium(III) catalyst.



Scheme 4 Proposed mechanism.

Importantly, the obtained 2-(2-hydroxyphenyl)-2-alkoxymalonates could serve as useful platforms for further synthetic manipulations. As illustrated in Scheme 5, product **3a** could undergo an esterlysis/decarboxylation in the presence of LiOH to give the valuable ethyl 2-hydroxy-α-methoxy-benzenacetate **5a**. In addition, product **3a** also could produce the important **6a** through a standrad intramolecular-transesterification. Further transformation of **6a** *via* an esterlysis/decarboxylation process yielded the 3-substituted benzofuran-2(3*H*)-one **7a**, a very valuable skeleton in natural products and biologically active compounds.[12]



Scheme 5 Derivatization of **3a**.

In summary, we have developed the first example of Rh(III)-catalyzed and alcohol-involved carbenoid C–H insertion (*ortho*-alkylation) of *N*-phenoxyacetamides by α-diazomalonates for direct and highly efficient synthesis of privileged 2-(2-hydroxyphenyl)-2-alkoxymalonates with a α-quaternary carbon center and free-OH moiety, in which O–NHAc group was employed as the versatile ODG. Considering the valuable structures of the products, mild reaction conditions, and good substrate/functional group tolerance, the reaction should have potential of wide synthetic utility.

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Notes and references

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†Electronic Supplementary Information (ESI) available: Detailed experimental procedure and characterization data of all new compounds. See DOI: 10.1039/b000000x/

1 For selected reviews, see: (a) G. Song, F. Wang and X. Li, *Chem. Soc. Rev.*, 2012, **41**, 3651; (b) D. A. Colby, A. S. Tsai, R. G. Bergman and J. A. Ellman, *Acc. Chem. Res.*, 2012, **45**, 814; (c) C. Zhu, R. Wang and J. R. Falck, *Chem. –Asian J.*, 2012, **7**, 1502; (d) N. Kuhl, M. N. Hopkinson, J. Wencel-Delord and F. Glorius, *Angew. Chem., Int. Ed.*, 2012, **51**, 10236; (e) S. R. Neufeldt and M. S. Sanford, *Acc. Chem. Res.*, 2012, **45**, 936; (f) S. I. Kozhushkov and L. Ackermann, *Chem. Sci.*, 2013, **4**, 886; (g) J. Wencel-Delord and F. Glorius, *Nat. Chem.*, 2013, **5**, 369; (h) V. S. Thirunavukkarasu, S. I. Kozhushkov and L. Ackermann, *Chem. Commun.*, 2014, **50**, 29; (i) L. Ackermann, *Acc. Chem. Res.*, 2014, **47**, 281; (j) N. Kuhl, N. Schröder and F. Glorius, *Adv. Synth. Catal.*, 2014, **356**, 1443; (k) Y. Zhang, X. Jie, H. Zhao, G. Li and W. Su, *Org. Chem. Front.*, 2014, **1**, 843; (l) C. X. Zhuo, C. Zheng and S. L. You, *Acc. Chem. Res.*, 2014, **47**, 2558; (m) F. Chen, T. Wang and N. Jiao, *Chem. Rev.*, 2014, **114**, 8613; (n) R. He, Z. T. Huang, Q. Y. Zheng, C. Wang, *Tetrahedron Lett.*, 2014, **55**, 5705.
2 F. W. Patureau and F. Glorius, *Angew. Chem., Int. Ed.*, 2011, **50**, 1977.

3 For selected examples on C–H activation by using N–OR groups as ODGs, see: (a) J. Wu, X. Cui, L. Chen, G. Jiang and Y. Wu, *J. Am. Chem. Soc.*, 2009, **131**, 13888; (b) S. Rakshit, C. Grohmann, T. Besset and F. Glorius, *J. Am. Chem. Soc.*, 2011, **133**, 2350; (c) T. K. Hyster and T. Rovis, *Chem. Commun.*, 2011, **47**, 11846; (d) X. Zhang, D. Chen, M. Zhao, J.Zhao, A. Jia and X. Li, *Adv. Synth. Catal.*, 2011, **353**, 719; (e) N. Guimond, S. I. Gorelsky and K. Fagnou, *J. Am. Chem. Soc.*, 2011, **133**, 6449; (f) C. Kornhaaβ, J. Li and L. Ackermann, *J. Org. Chem.*, 2012, **77**, 9190; (g) H. Wang and F. Glorius, *Angew. Chem., Int. Ed.*, 2012, **51**, 7318; (h) T. K. Hyster, K L. Knörr, T. R. Ward and T. Rovis, *Science*, 2012, **338**, 500; (i) H. Wang, C. Grohmann, C. Nimphius and F. Glorius, *J. Am. Chem. Soc.*, 2012, **134**, 19592; (j) B. Ye and N. Cramer, *Science*, 2012, **338**, 504; (k) T. K. Hyster, K. E. Ruhl and T. Rovis, *J. Am. Chem. Soc.*, 2013, **135**, 5364; (l) S. Cui, Y. Zhang, D. Wang and Q. Wu, *Chem. Sci.*, 2013, **4**, 3912; (m) X. Huang, J. Huang, C. Du,; X. Zhang, F. Song and J. You, *Angew. Chem., Int. Ed.*, 2013, **52**, 12970; (n) U. Sharma, Y. Park and S. Chang, *J. Org. Chem.*, 2014, **79**, 9899; (o) D. Zhao, F. Lied and F. Glorius, *Chem. Sci.*, 2014, **5**, 2869; (p) D. G. Yu, F. de Azambuja, T. Gensch, C. G. Daniliuc and F. Glorius, *Angew. Chem., Int. Ed.*, 2014, **53**, 9650; (q) X. Zhang, Z. Qi and X. Li, *Angew. Chem., Int. Ed.*, 2014, **53**, 10794; (r) J. M. Neely and T. Rovis, *J. Am. Chem. Soc.*, 2014, **136**, 2735; (s) Y. J. Liu, H. Xu. W. J. Kong, M. Shang, H. X. Dai and J. Q. Yu, *Nature*, 2014, **515**, 389.

4 For selected examples on C–H activation by using N–NR groups as ODGs, see: (a) D. Zhao, Z. Shi and F. Glorius, *Angew. Chem., Int. Ed.*, 2013, **52**, 12426; (b) C. Wang and Y. Huang, *Org. Lett.*, 2013, **15**, 5294; (c) B. Liu, C. Song, C. Sun, S. Zhou and J. Zhu, *J. Am. Chem. Soc.*, 2013, **135**, 16625; (d) C. Wang, H. Sun, Y. Fang and Y. Huang, *Angew. Chem., Int. Ed.*, 2013, **52**, 5795; (e) L. Zheng and R. Hua, *Chem. −Eur. J.*, 2014, **20**, 2352; (f) K. Muralirajan, C. H. Cheng, *Adv. Synth. Catal.*, 2014, **356**, 1571; (g) T. Matsuda and Y. Tomaru, *Tetrahedron Lett.*, 2014, **55**, 3302; (h) Z. Zhang, H. Jiang and Y. Huang, *Org. Lett.*, 2014, **16**, 5976; (i) H. Sun, C.Wang, Y. F. Yang, P. Chen, Y. D. Wu, X. Zhang and Y. Huang, *J. Org. Chem.*, 2014, **79**, 11863; (j) B. Zhou, J. Du, Y.Yang and Y. Li, *Chem. −Eur. J.*, 2014, **20**, 12768; (k) B. Zhou, Y. Yang, H. Tang, J. Du, H. Feng and Y. Li, *Org. Lett.*, 2014, **16**, 3900.

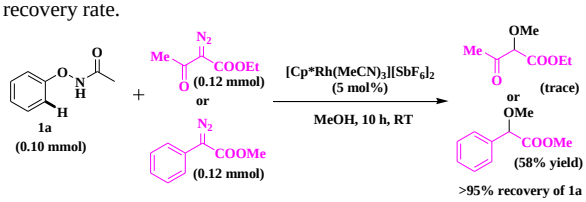
5 For selected examples on C–H activation by using O–NAc group as a ODG, see: (a) G. Liu, Y. Shen, Z. Zhou and X. Lu, *Angew. Chem., Int. Ed.*, 2013, **52**, 6033; (b) Y. Shen, G. Liu, Z. Zhou and X. Lu, *Org. Lett.*, 2013, **15**, 3366; (c) F. Hu, Y. Xia, F. Ye, Z. Liu, C. Ma, Y. Zhang and J. Wang, *Angew. Chem.*, 2014, **126**, 1388; (d) H. Zhang, K. Wang, B. Wang, H. Yi, F. Hu, C. Li, Y. Zhang and J. Wang, *Angew. Chem., Int. Ed.*, 2014, **53**, 13234; (e) P. Duan, X. Lan, Y. Chen, S. S. Qian, J. J. Li, L. Lu, Y. Lu, B. Chen, M. Hong and J. Zhao, *Chem. Commun.*, 2014, **50**, 12135; (f) Y. Chen, D. Wang, P. Duan, R. Ben, L. Dai, X. Shao, M. Hong, J. Zhao and Y. Huang, *Nat. Commun.*, 2014, **5**, 4610.

6 For selected reviews, see: (a) Z. Zhang and J. Wang, *Tetrahedron*, 2008, **64**, 6577; (b) H. M. L. Davies and J. R. Manning, *Nature*, 2008, **451**, 417; (c) M. P. Doyle, R. Duffy, M. Ratnikov, L. Zhou, *Chem. Rev.* 2010, **110**, 704; (d) Y. Zhang and J. Wang, *Eur. J. Org. Chem.* **2011**, 1015; (e) J. Barluenga and C. Valdés, *Angew. Chem., Int. Ed.*, 2011, **50**, 7486; (f) Z. Shao and H. Zhang, *Chem. Soc. Rev.*, 2012, **41**, 560; (g) Q. Xiao, Y. Zhang and J. Wang, *Acc. Chem. Res.*, 2013, **46**, 236; (h) Z. Liu and J. Wang, *J. Org. Chem.*, 2013, **78**, 10024; (i) Y. Xia, Y. Zhang and J. Wang, *ACS Catal.*, 2013, **3**, 2586.

7 For representative examples on Rh(III)-catalyzed carbenoid C–H insertion reactions, see: (a) W. W. Chan, S. F. Lo, Z. Zhou and W. Y. Yu, *J. Am. Chem. Soc.* 2012, **134**, 13565; (b) Z. Shi, D. C. Koester, M. Boultadakis-Arapinis and F. Glorius, *J. Am. Chem. Soc.*, 2013, **135**, 12204; (c) X. Yu, S. Yu, J. Xiao, B. Wan and X. Li, *J. Org. Chem.*, 2013, **78**, 5444; (d) S. Yu, S. Liu, Y. Lan, B. Wan and X. Li, *J. Am. Chem. Soc.*, 2015, DOI: 10.1021/ja511796h; (e) Y. Zhang, J. Zheng and S. Cui, *J. Org. Chem.*, 2014, **79**, 6490; (f) H. W. Lam, K. Y. Man, W. W. Chan, Z. Zhou and W. Y. Yu, *Org. Biomol. Chem.*, 2014, **12**, 4112; (g) Y. Liang, K. Yu, B. Li, S. Xu, H. Song and B. Wang, *Chem. Commun.*, 2014, **50**, 6130; (h) F. Hu, Y. Xia, F. Ye, Z. Liu, C. Ma, Y. Zhang and J. Wang, *Angew. Chem., Int. Ed.*, 2014, **53**, 1364; (i) J. Jeong, P. Patel, H. Hwang and S. Chang, *Org. Lett.*, 2014, **16**, 4598; (j) W. Ai, X. Yang, Y. Wu, X. Wang, Y. Li, Y. Yang and B. Zhou, *Chem. −Eur. J.*, 2014, **20**, 17653; (k) B. Ye and N. Cramer, *Angew. Chem., Int. Ed.*, 2014, **53**, 7896; (l) X. G. Li, M. Sun, K. Liu, Q. Jin and P. N. Liu, *Chem. Commun.*, 2015, DOI: 10.1039/c4cc09314c; (m) J. Shi, Y. Yan, Q. Li, H. E. Xu and W. Yi, *Chem. Commun.*, 2014, **50**, 6483; (n) J. Shi, J. Zhou, Y. Yan, J. Jia, X. Liu, H, Song, H. E. Xu and W. Yi, *Chem. Commun.*, 2015, **51,** 668.

8 For the representative examples, see: (a) N. Guimond and K. Fagnou, *J. Am. Chem. Soc.*, 2009, **131**, 12050; (b) D. R. Stuart, P. Alsabeh, M. Kuhn and K. Fagnou, *J. Am. Chem. Soc.*, 2010, **132**, 18326; (c) D. J. Schipper, M. Hutchinson and K. Fagnou, *J. Am. Chem. Soc.*, 2010, **132**, 6910; (d) M. P. Huestis, L. Chan, D. R. Stuart and K. Fagnou, *Angew. Chem., Int. Ed.*, 2011, **50**, 1338; (e) J. Shi, B. Zhou, Y. Yang and Y. Li, *Org. Biomol. Chem.*, 2012, **10**, 8953; (f) W. Zhen, F. Wang, M. Zhao, Z. Du and X. Li, *Angew. Chem. Int. Ed.*, 2012, **51**, 11819; (g) Y. Chen, F. Wang, W. Zhen, X. Li, *Adv. Synth. Catal.*, 2013, **355**, 353; (h) D. S. Kim, J. W. Park and C. H. Jun, *Adv. Synth. Catal.*, 2013, **355**, 2667; (i) T. Gong, B. Xiao, W. Cheng, W. Su, J. Xu, Z. Liu, L. Liu and Y. Fu, *J. Am. Chem. Soc.*, 2013, **135**, 10630; (j) Y. Lian, J. R. Hummel, R. G. Bergman, J. A. Ellman, *J. Am. Chem. Soc.*, 2013, **135**, 12548; (k) K. Nobushige, K. Hirano, T. Satoh and M. Miura, *Org. Lett.*, 2014, **16**, 1188; (l) D. G. Yu, F. de Azambuja and F. Glorius, *Angew. Chem., Int. Ed.*, 2014, **53**, 2754.

9 Ethyl diazoacetoacetate and methyl 2-diazo-2-phenylacetate were also tested. The results showed that the reaction of ethyl diazoacetoacetate or methyl 2-diazo-2-phenylacetate and MeOH was occurred to give ethyl 2-methoxy-3-oxobutanoate (trace) and methyl 2-methoxy-2-phenylacetate (58% isolated yield), respectively, where substrate **1a** was retained perfectly with over 95% recovery rate.



10 For selected rhodium involved cleavage of aromatic C–H bonds through CMD way, see: (a) T. K. Hyster and T. Rovis, *J. Am. Chem. Soc.*, 2010, **132**, 10565; (b) L. Ackermann, *Chem. Rev.*, 2011, **111**, 1315; (c) H. Wang and F. Glorius, *Angew. Chem., Int. Ed.*, 2012, **51**, 7318; (d) J. Zheng and S. L. You, *Chem. Commun.*, 2014, **50**, 8204.

11 (a) K. B. Eisenthal, N. J. Turro, E. V. Sitzmann, I. R. Gould, G. Hefferon, J. Langan and Y. Cha, *Tetrahedron*, 1985, **41**, 1543; (b) D. A. Modarelli, S. Morgan and M. S. Platz, *J. Am. Chem. Soc.*, 1992, **114**, 7034; (c) V. V. Shevchenko, N. G. Zhegalova, A. O. Borzenko and V. A. Nikolaev, *Helv. Chem. Acta*, 2008, **91**, 501. (d) W. S. Jenks, M. J. Heying and E. M. Rockafellow, *Org. Lett.*, 2009, **11**, 955; (e) P. J. Davis, L. Harris, A. Karim, A. L. Thompson, M. Gilpin, M. G. Moloney, M. J. Pound and C. Thompson, *Tetrahedron Lett.*, 2011, **52**, 1553.

12 (a) A. Closse, W. Haefliger and D. Hauser, *J. Med. Chem.*, 1981, **24**, 1465; (b) W. D. Inman, J. Luo, S. D. Jolad, S.R. King and R. Cooper, *J. Nat. Prod.*, 1999, **62**, 1088; (c) M. L. Garduño-Ramírez, A. Trejo, V. Navarro, R. Bye, E. Linares and G. Delgado, *J. Nat. Prod.*, 2001, **64**, 432; (d) G. D. Huang, Y. J. Yang, W. S. Wu and Y. Zhu, *J. Nat. Prod.*, 2010, **73**, 1954; (e) L. J. Wang, J. Xiong, S. T. Liu and J. F. Hu, *Chem. Biodivers.*, 2014, **11**, 919.