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Single-atom skeletal editing of 2*H*-indazoles enabled by difluorocarbene

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A novel difluorocarbene promoted single-atom skeletal editing of 2*H*-indazoles is demonstrated herein. Ethyl bromodifluoroacetate was severed as the difluorocarbene source in the current protocol, facilitating the cleavage of the N–N bond *via* carbon atom insertion. This metal-free ring expansion reaction enables the late-stage diversification of indazole skeletons, assembling a diverse array of functionalized quinazolin-4(3*H*)-ones in decent yields with excellent functional group compatibility.

indazoles, skeletal editing, difluorocarbene, N–N bond cleavage, quinazolin-4(3*H*)-ones

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Since molecular editing contributes to the ability to enact chemical transformations in a concise and chemospecific fashion, it has indisputably represented the robust platform for modern approaches to drug discovery and life sciences [1]. In general, ornament of an exocyclic atom such as functionalization of C–H or C–X bonds is preferably deemed as peripheral editing. While altering the atomic composition that comprises a ring system can be construed as molecular skeletal editing (Scheme 1a). With respect to skeletal editing, single-atom modification of the ring structure has loomed as the most elementary of feasible changes to a molecular framework in chemical precision, which just manipulations the ring texture by one atom without regard to the cases of the exocyclic functional groups. The classical Tiffeneau-Demjano [2], Ciamician-Dennstedt [3] and Gabriel-Colman [4] rearrangement as well as the Bayer-Villiger [5], Beckmann [6] and Favorskii [7] rearrangement of cyclic compounds are known paradigm for such single-atom skeletal editing. Throughout previously documented transformations, there are three situations for single-atom molecular skeletal editing: (a) ring expansion ($n \rightarrow n+1$) [8]; (b) ring contraction ($n \rightarrow n-1$) [9]; (c) the transmutation of one atom of an integral part for another [10] (Scheme 1b). In consideration of the retrosynthetic simplicity, single-atom logic skeletal editing has emerged as fertile territory for the evolution of novel and formidable synthetic transformations. Given the capacity to surmount the traditional hurdles in pharmaceutic exploitation at late-stage, the development of a novel and promising platform for single-atom skeletal editing is still in great demand in the realm of both chemistry and drug discovery.

To fulfill the single-atom skeletal editing of (hetero)cyclic ring system, carbene has the inherent peculiarity for the ornament of the molecular skeleton. A variety of prominent nitrene- and carbene-induced transformations have been innovated *via the* insertion of retrosynthetic disconnection of the structural motifs and cores [11–13]. For instance, in

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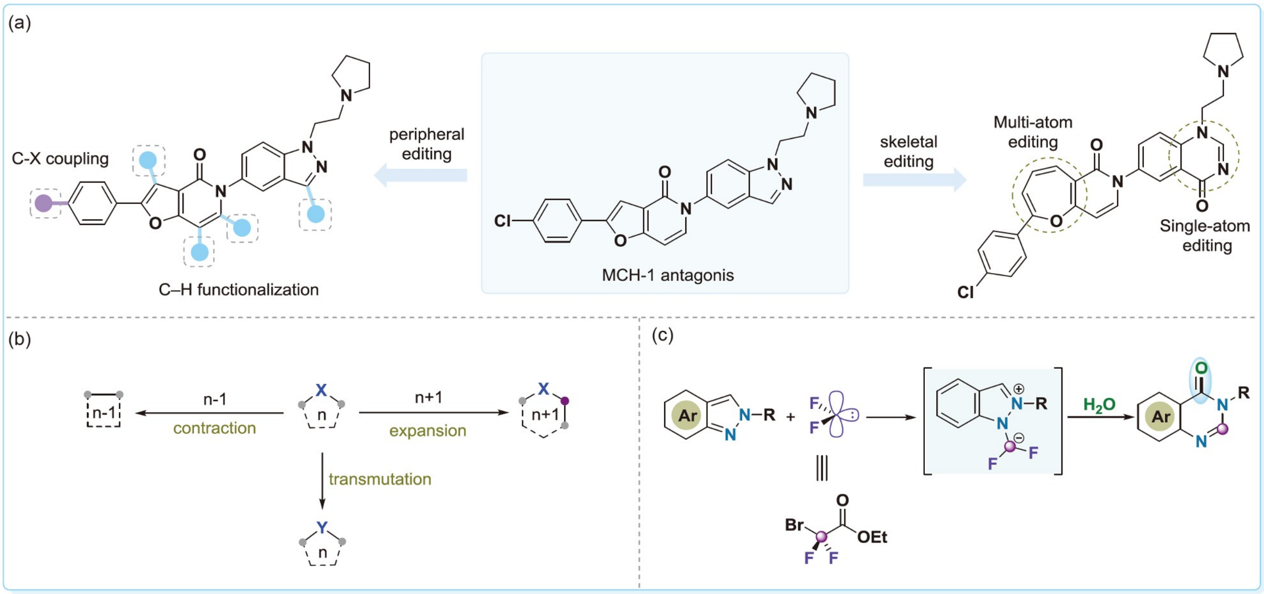
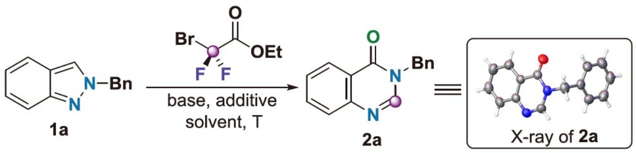


Scheme 1 (a) Examples of peripheral editing and skeletal editing; (b) classification of single-atom skeletal editing; (c) difluorocarbene promoted single-atom skeletal editing of 2*H*-Indazoles (this work) (color online).

2021, Levin's group [12] described a preeminent chlorodiazirines-promoted carbon atom insertion into pyrroles and indoles. During our preparation of this manuscript, the same group also demonstrated an outstanding single-atom skeletal editing reaction of pyrazole and indazole to forge diverse pyrimidines and quinazolines [13]. Despite the known outstanding contributions for skeletal editing of (hetero)cyclic ring system enabled by carbene, there is an astounding dearth of difluorocarbene-mediated modification of the ring size of carbocyclic or heterocyclic frameworks. Owing to the high electron deficiency, difluorocarbene represents the versatile reactive species [14], which has been frequently utilized as the vigorous difluoromethylenating reagent [15], difluoromethylating reagent [16,17], carbonyl source [18], C1 synthon [19,20] and so forth. In sharp contrast to previous decorations of difluorocarbene for the construction of fluorinated or non-fluorinated products, difluorocarbene involved skeletal editing of the ring system has never been documented heretofore. Herein, we present an expedient difluorocarbene-mediated single-atom skeletal editing of 2*H*-indazoles *via* insertion into the N–N bond, enabling the streamline synthesis of quinazolin-4(3*H*)-ones [21] under metal- and oxidant-free conditions (Scheme 1c).

To commence the proof-concept study, the treatment of 2-benzyl-2*H*-indazole (**1a**) with $BrCF_2COOEt$ was conducted as the model reaction. When the model reaction proceeded in CH_3CN by using K_3PO_4 as the base, the ring-expansion product 3-benzylquinazolin-4(3*H*)-one **2a** was indeed gained in 58% yield, the structure of which was unequivocally ascertained by X-ray single crystal diffraction (CCDC: 2215093). Encouraged by this result, a battery of solvents was then inspected (Table 1, entries 2–4), which turned out CH_3CN was still the best reaction medium to facilitate the N–N bond cleavage of 2*H*-indazoles. In consideration of the source of oxygen in the desired quinazolin-4(3*H*)-ones,

Table 1 Optimization of reaction conditions[a)]



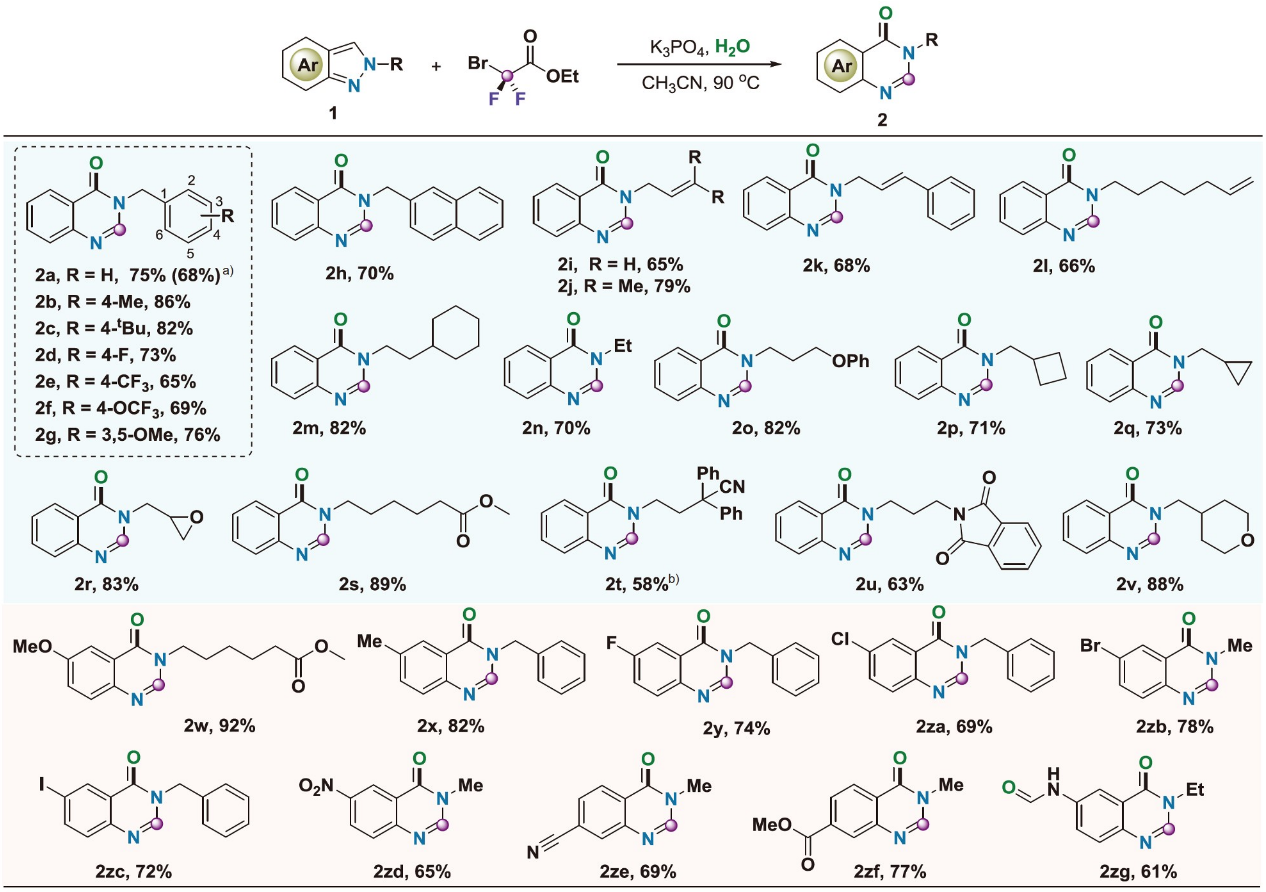
Entry	Base	Solvent	Additive[c)]	T (°C)	Yield (%)[b)]
1	K_3PO_4	CH_3CN	–	90	58
2	K_3PO_4	PhMe	–	90	30
3	K_3PO_4	EtOAc	–	90	41
4	K_3PO_4	1,4-Dioxane	–	90	25
5	K_3PO_4	CH_3CN	TBHP	90	63
6	K_3PO_4	CH_3CN	H_2O	90	75
7	K_3PO_4	CH_3CN	CAN	90	trace
8	K_2CO_3	CH_3CN	H_2O	90	65
9	Na_2CO_3	CH_3CN	H_2O	90	61
10	Cs_2CO_3	CH_3CN	H_2O	90	54
11	KH_2PO_4	CH_3CN	H_2O	90	60
12	K_3PO_4	CH_3CN	H_2O	RT	0
13	K_3PO_4	CH_3CN	H_2O	70	52
14[d)]	K_3PO_4	CH_3CN	H_2O	90	23

a) **1a** (0.3 mmol), $BrCF_2COOEt$ (0.9 mmol), base (0.9 mmol), solvent (2 mL), 16 h. b) isolated yields. c) 0.9 mmol of additive was added. d) 3 mmol of H_2O was used. TBHP = *tert*-Butyl hydroperoxide. CAN = Cerium(IV) ammonium nitrate.

several additives were added to this reaction system (Table 1, entries 5–7). To our delight, the yield of **2a** was increased to 75% when 3 equivalents of H_2O were served as the additive (Table 1, entry 6). Subsequently, a suite of inorganic bases was examined (Table 1, entries 8–11). However, the results showcased that no evident improvements were gained when K_3PO_4 was replaced by other inorganic bases. As the following optimization, we also screened the effect of reaction temperature, which indicated that the optimal choice for this skeletal editing of 2*H*-indazoles was still carried out at 90 °C (Table 1, entries 12–13). Since the water could slightly accelerate this N–N bond cleavage of 2*H*-indazoles, the amount of water was also investigated. When we increased the amount of water, despondently, the inferior yield of 3-benzylquinazolin-4(3*H*)-one **2a** was acquired (Table 1, entry 14).

Given that the optimum reaction conditions have been established, the generality of this difluorocarbene-induced skeletal editing of 2*H*-indazoles was then perused. As summarized in Scheme 2, a sequence of functionalized 2-benzyl-2*H*-indazoles bearing different electronic properties on the benzyl group displayed good reactivity in this transformation, enabling the production of 3-benzylquinazolin-4(3*H*)-ones (**2b**–**2g**) in 65%–86% yields. Sterically demanding 2-(naphthalen-2-ylmethyl)-2*H*-indazole (**1h**) was proven to be a good candidate as well, affording the targeted quinazolin-4(3*H*)-one **2h** in 70% yield. Rejoicingly, a suite of N-substituted 2*H*-indazoles installed on the alkenyl were also amenable to this difluorocarbene-mediated ring-expansion reaction and the desired products (**2i**–**2l**) were isolated in decent yields under the identified conditions. 2*H*-indazoles tethered with N-substituted cyclic or chain alkanes and heterocycles (**1m**–**1v**) could also be engaged in this N–N bond cleavage reaction, delivering the expected quinazolin-4(3*H*)-ones **2m**–**2v** in 58%–89% yields.

Next, we focused on the scope with respect to the substituents on the aromatic ring of the indazole skeleton. 2*H*-Indazoles having the electron-donating functionality demonstrated excellent activity in this carbon atom insertion reaction and the desired products **2w** and **2x** could be readily obtained in 92% and 82% yields, respectively. Halo-aromatic substituted 2*H*-indazoles, such as fluoro, chloro, bromo and iodo groups, were also well compatible under this difluorocarbene-involved ring expansion reaction, affording

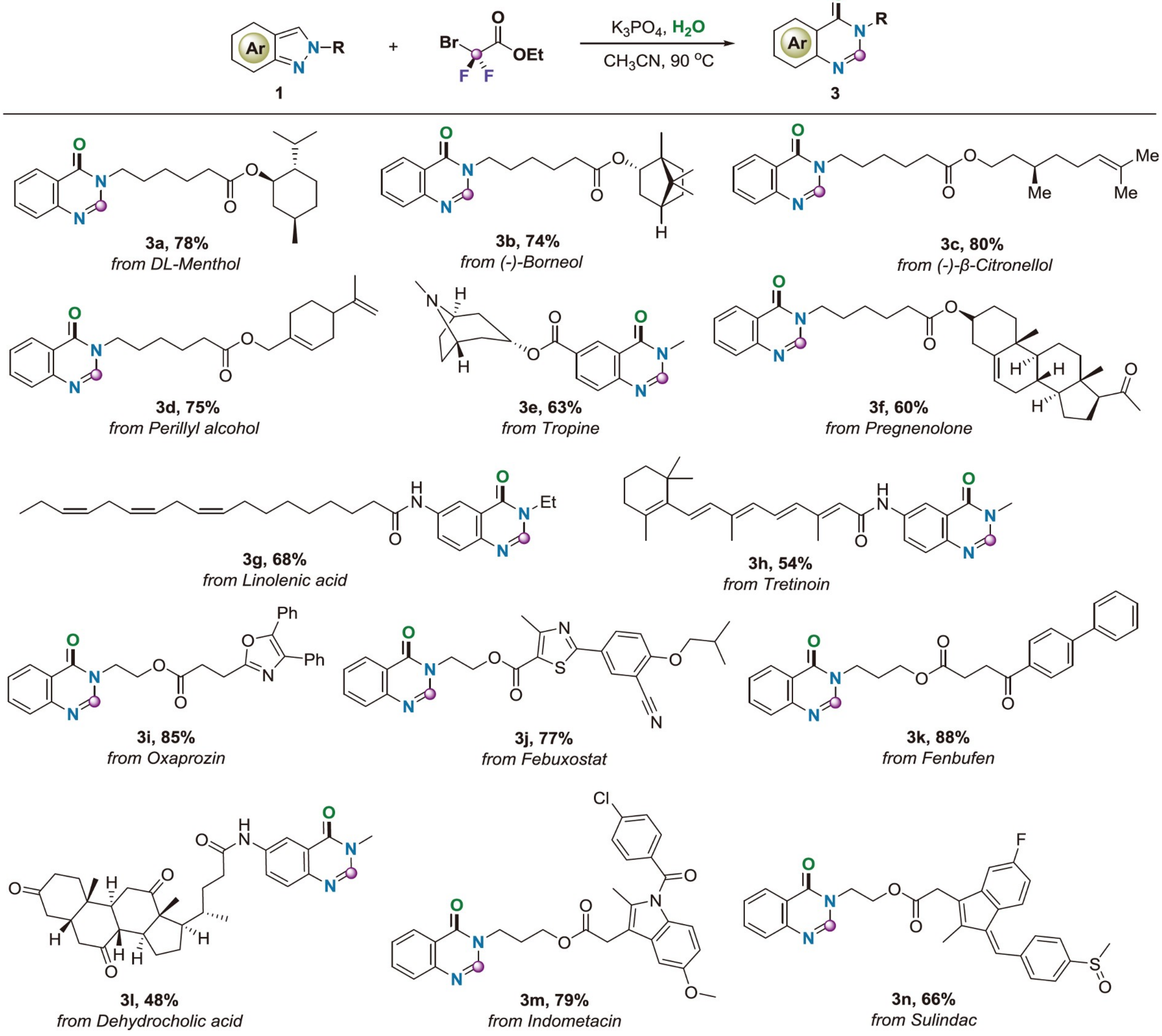


All reactions unless otherwise stated were carried out with 1 (0.3 mmol), $BrCF_2COOEt$ (0.9 mmol), H_2O (0.9 mmol) and K_3PO_4 (0.9 mmol) in CH_3CN (2 mL) heated at 90 °C for 16 h. Yields of isolated products were reported. a) 5 mmol scale. b) the reaction was conducted at 100 °C.

Scheme 2 Substrate scope for the assembly of quinazolin-4(3*H*)-ones (color online).

the halo-substituted quinazolin-4(3*H*)-ones (**2y**, **2za**–**2zc**) in modest yields. In addition, the aromatic ring of 2*H*-indazoles mounted on electron-withdrawing groups was also found to react with $BrCF_2COOEt$ smoothly and the corresponding quinazolin-4(3*H*)-ones (**2zd**–**2zf**) could be achieved in 65%–77% yields. When 2-ethyl-2*H*-indazol-5-amine was subjected to this reaction system, difluorocarbene not only prompted the N–N bond cleavage of the indazole skeleton but also elaborated the free NH_2 group to formamide [18a,18b] under this basic conditions, giving the production of *N*-(3-ethyl-4-oxo-3,4-dihydroquinazolin-6-yl)formamide (**2zg**) in 61% yield. The scalability of this difluorocarbene induced N–N bond deconstructive reaction was also assessed. Treatment of 5 mmol of **1a** with $BrCF_2COOEt$ under these identified conditions enables to assemble 3-benzyl-quinazolin-4(3*H*)-one **2a** in 68% yield without loss of efficacy.

To further illustrate the potential of the reaction for expanding the accessible chemical space, the current method was then applied to remodel 2*H*-indazoles containing bioactive and pharmaceutical molecules, which was summarized in Scheme 3. Gratifyingly, a sequence of natural product alcohols, such as DL-Menthol, (−)-Borneol, (−)-β-Citronellol, Perillyl alcohol, Tropine and Pregnenolone, could be successfully incorporated into the 2*H*-indazoles. And all of them enabled the generation of corresponding quinazolin-4(3*H*)-ones **3a**–**3f** in 60%–80% yields under this metal-free ring expansion reaction. To further extrapolate the late-stage modifications of 2*H*-indazoles, a suite of 2*H*-indazoles derived from structurally complicated carboxylic acids pharmaceutical molecules, such as Linolenic acid, Tretinoin, Oxaprozin, Febuxostat, Fenbufen, Dehydrocholic

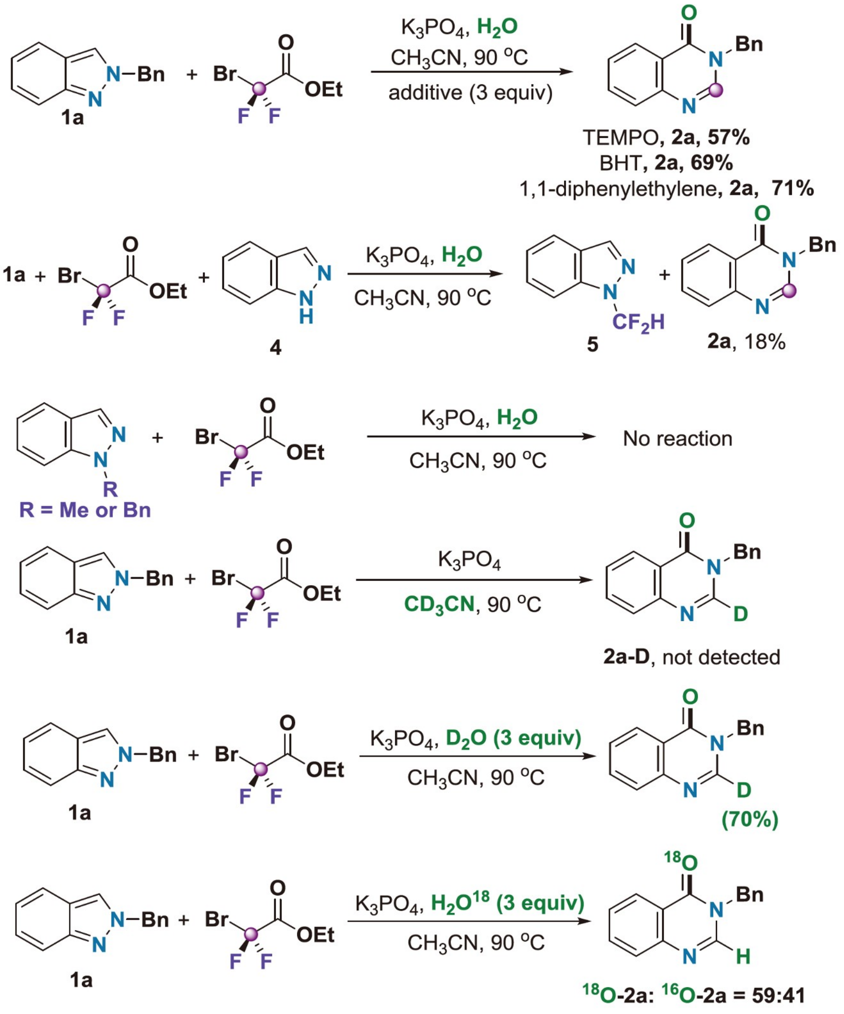


All reactions unless otherwise stated were carried out with 1 (0.3 mmol), $BrCF_2COOEt$ (0.9 mmol), H_2O (0.9 mmol) and K_3PO_4 (0.9 mmol) in CH_3CN (2 mL) heated at 90 °C for 16 h. Yields of isolated products were reported.

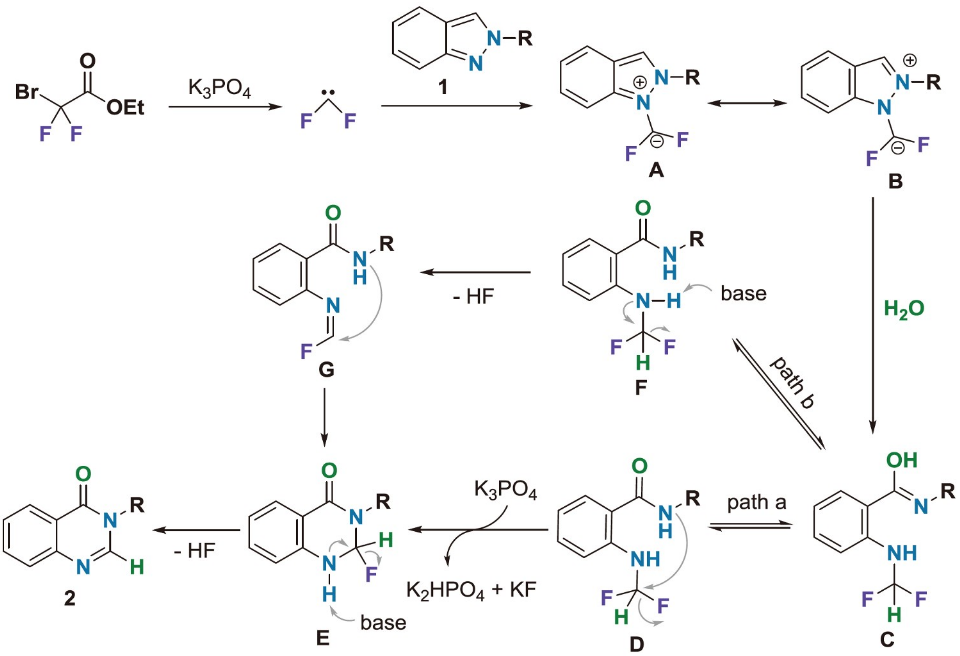
Scheme 3 Synthesis of quinazolin-4(3*H*)-ones bearing bioactive and drug molecules (color online).

acid, Indometacin and Sulindac, were also engaged in this difluorocarbene promoted skeletal editing reaction and the expected products **3g**–**3n** could be readily gained in synthetically acceptable yields. The above results reveal that the current synthetic methodology not only showcased commendable functional group tolerance, but also enabled the capacity for the streamline construction of bioactive quinazolin-4(3*H*)-ones.

As the following-up investigations, a suite of experiments was conducted to gain mechanistic insight into this difluorocarbene-promoted skeletal editing reaction of 2*H*-indazoles (Scheme 4). When 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), 2,6-di-*tert*-butyl-4-methylphenol (BHT) and 1,1-diphenylethylene were added as radical scavengers in this reaction, the ring-expansion of 2*H*-indazoles could also work smoothly and the desired quinazolin-4(3*H*)-one **2a** were still obtained in good yields (Scheme 4a), which possibly eliminated a radical-type reaction regime for this N–N bond cleavage of 2*H*-indazoles. When carbene trapping reagent indazole **4** was subjected to this reaction, the 1-(difluoromethyl)-1*H*-indazole **5** was detected as the major product by GC-MS and a relatively lower yield of **2a** was observed (Scheme 4b). We were curious to understand whether 1*H*-indazole derivatives could be converted in this reaction system. A number of 1*H*-indazoles were prepared and submitted to these metal-free conditions. However, when N-substituted 1*H*-indazoles were deemed as the starting materials, no skeletal editing reactions of 1*H*-indazoles were observed under these established conditions (Scheme 4c). To affirm the source of hydrogen in the imine entity of quinazolin-4(3*H*)-one, deuterium labeling experiments were then carried out. When the model reaction proceeded in CD_3CN without adding water, no deuteration of 3-benzylquinazolin-4(3*H*)-one was detected (Scheme 4d). When **1a** reacted with $BrCF_2COOEt$ by adding 3 equivalents of D_2O as the adscititious reagent, 70% deuteration of **2a** was detected at the C–H bond of imine (Scheme 4e). Subsequently, an isotope labeling experiment was also executed to confirm the origination of the carbonyl oxygen atom of the targeted quinazolin-4(3*H*)-ones. When this N–N bond cleavage reaction



Scheme 4 Primary mechanism studies (color online).



Scheme 5 Plausible reaction mechanism (color online).

was performed by employing 3 equivalents of $H_2{}^{18}O$ as the accelerant, 59% of ^{18}O-labeled quinazolin-4(3*H*)-one **2a** was detected (Scheme 4f). These results manifested that both the hydrogen of the imine entity and the oxygen of the carbonyl group should derive from water.

According to previous work and the above empirical data, a plausible reaction mechanism for this metal-free skeletal editing reaction *via* disconnection of 2*H*-indazoles is delineated in Scheme 5. First, difluorocarbene (:CF_2) is formed *in-situ via* base-promoted double cleavage of $BrCF_2COOEt$ [20]. Subsequently, the *in-situ* generated difluorocarbene species is captured by 2*H*-indazole **1** to afford the intermediate **A** or it is resonant structure **B**. This imine carbocation **B** is further attacked by water to provide the ring-opening intermediate **C** *via* the N–N bond cleavage of 2*H*-indazoles. Later on, the amide compound **D** goes through the intramolecular nucleophilic attack, delivering compound **E** *via* C–F bond scission. Since the group of NH-CF_2H is unstable, another alternative pathway for the production of compound **E** is showcased as path b in Scheme 5. Defluorination of intermediate **F** enables to deliver the intermediate **G** bearing an N=CFH moiety, which subsequently is attacked by another nitrogen to render the intermediate **E**. With the assistance of base, further defluorination of compound **E** furnishes the desired product quinazolin-4(3*H*)-ones **2**.

In conclusion, we have discovered a novel single-atom skeletal editing of 2*H*-Indazoles promoted by difluorocarbene. This difluorocarbene-induced N–N bond cleavage of 2H-indazoles endows a new platform for the streamline assembly of functionalized quinazolin-4(3*H*)-ones *via* late-stage functionalizations. The current protocol features such as metal-free, oxidant-free, user-friendly operation, good yields and broad substrate scope as well as valuable products. Furthermore, this ring expansion reaction can be easily amplified without loss of effectiveness. Further synthetic applications of difluorocarbene induced skeletal editing reactions are in progress in our laboratory.

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Conflict of interest The authors declare no conflict of interest.

Supporting information The supporting information is available online at chem.scichina.com and link.springer.com/journal/11426. The supporting materials are published as submitted, without typesetting or editing. The responsibility for scientific accuracy and content remains entirely with the authors.

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