Wiley Analytical Science

Automating the Laboratory: Maximizing Efficiency Through Smart Solutions

April 27, 9:00am - 10:00am EDT

Automation has reached ever larger areas recently. Due to the development of numerous new, cost-effective automation devices and modules, the automation of laboratory processes is also of increasing interest to small and medium-sized companies and research laboratories. Different degrees of automation from the automation of individual sub-steps to partial automation and finally full automation without manual intervention by an operator are possible.

Watch this session during the WAS Virtual Conference:

Prof. Kerstin Thurow

Prof. Thole Züchner

Register Now

This talk is sponsored by SARTORIUS

RESEARCH ARTICLE doi.org/10.1002/adsc.202200903 Advanced Synthesis & Catalysis

Borane-Catalyzed, HFIP-Assisted Carbene Insertion into Internal Alkenyl C–H Bonds under Metal-Free Conditions

Zilong Huang,[a, b] Jie Lin,[a, b] Juan Ma,[a, b] Liandi Wang,[a] Yong-Gui Zhou,[a,*] and Zhengkun Yu[a, c,*]

[a] Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian, Liaoning 116023, People's Republic of China
E-mail: zkyu@dicp.ac.cn; ygzhou@dicp.ac.cn
[b] University of Chinese Academy of Sciences, Beijing 100049, People's Republic of China
[c] State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Road, Shanghai 200032, People's Republic of China

Manuscript received: August 18, 2022; Revised manuscript received: October 31, 2022;
Version of record online: November 28, 2022

Supporting information for this article is available on the WWW under https://doi.org/10.1002/adsc.202200903

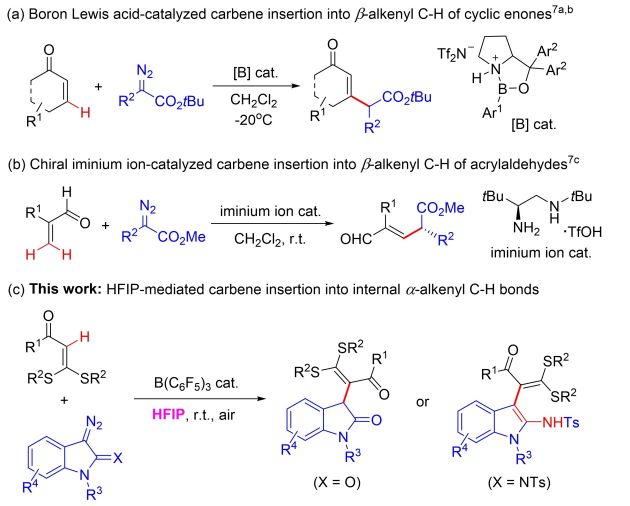
Abstract: Carbene insertion into the C(sp^2)–H bonds of internal alkenes was enabled in air by HFIP (1,1,1,3,3,3-hexafluoro-2-propanol) as both the mediator and solvent through its cooperation with borane $B(C_6F_5)_3$ as the catalyst. 3-Diazooxindoles and 3-diazoindolin-2-imines were amenable to work as the carbene precursors, and α-oxo ketene dithioacetals acted as the internal alkenes at ambient temperature. The present synthetic protocol features metal-free conditions, diverse substituent tolerance, and 47–84% yields, offering an efficient route to 3-vinylated oxindole and indole derivatives.

Keywords: carbene insertion; HFIP; $B(C_6F_5)_3$; diazo compounds; C–H functionalization

Introduction

C–H functionalization has emerged as a powerful method to access organic molecules.[1] Such a transformation can be achieved *via* carbene transfer or insertion into various C–H bonds by means of diazo compounds as the carbene precursors. In this area, efforts are generally devoted to the development of transition-metal-catalyzed carbene insertion reactions due to the high catalytic efficiency and catalyst diversity.[2] Metal carbenes have been proven to be the active species in carbene insertion into C(sp^2)–H bonds of arenes[3] and alkenes.[4] Although metal-free C–H functionalization has been a challenge in organic chemistry, metal-free C–H insertions have attracted continuous interest, in which carbene insertion into aryl and heteroaryl C–H bonds has been achieved with non-metallic catalysts.[5] In this regard, $B(C_6F_5)_3$ promoted carbene insertions to the C(sp^2)–H bonds of phenols,[6a] indoles,[6b] and carbazoles[6c] were reported. Compared to carbene insertion into aryl, heteroaryl, and alkyl C–H bonds, carbene insertion into alkenyl C–H bonds has been challenging because alkenes usually undergo cyclopropanation with a carbene species in the presence of a transition-metal catalyst. In 2013, Ryu group reported boron Lewis acid-catalyzed carbene insertion into β-alkenyl C–H bond of cyclic enones[7a,b] (Scheme 1a). In 2020, Luo, et al. applied iminium ion catalysis to achieve carbene insertion into β-alkenyl C–H bond of terminal alkenes, that is, acrylaldehydes[7c] (Scheme 1b). These methods were all explored by utilizing the electron-deficiency property of the β-alkenyl carbon in carbonyl compounds. Unfortunately, carbene insertion into the α-alkenyl C–H bond adjacent to a carbonyl still remains untouched.

1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP), a non-nucleophilic fluorinated alcohol with strong hydrogen-bonding donor property, has recently been used to promote a wide range of challenging chemical transformations.[8] HFIP as a solvent paired with a Lewis acid can promote transformations of carbonyl compounds,[9] epoxides,[10] alcohols,[11] phenols,[12a] halides,[12b] alkenes,[13,14] and alkynes.[15] For example, Leboeuf group achieved *ortho*-C–H alkylation of anilines with deactivated styrenes and unactivated alkenes[13a] and hydroarylation of deactivated styrenes with arenes[13b] through the cooperation between



Scheme 1. Metal-free carbene insertion into alkenyl C–H bonds.

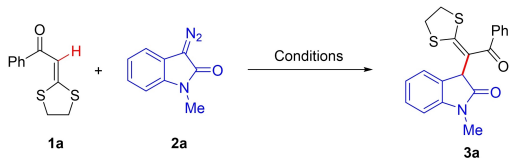
calcium(II) triflimide catalyst and HFIP solvent. Colomer realized *para*-C–H alkylation of anilines with alkenes under NaOAc catalysis in HFIP.[14] DFT calculations and experimental studies have revealed that Lewis acid $B(C_6F_5)_3$ either facilitates carbene generation from donor-acceptor diazo compounds or promote carbenium ion generation for autocatalytic pyrazole formation.[16]

During the continuous investigation of alkenyl C–H functionalization,[17,18] we envisioned that a combination of Lewis acid $B(C_6F_5)_3$ as the catalyst and HFIP as the mediator might be applied in carbene insertion into C–H bonds of internal alkenes, that is, α-oxo ketene dithioacetals, under metal-free conditions, which will be a supplement to transition-metal-catalyzed carbene insertion into alkenyl C–H bonds. Herein, we disclose $B(C_6F_5)_3$-catalyzed, HFIP-mediated carbene insertion into α-alkenyl C–H bonds of α-oxo ketene dithioacetals, a class of polarized internal alkenes (Scheme 1c).

Results and Discussion

Initially, the reaction of internal alkene, that is, α-oxo ketene dithioacetal (**1a**), and diazo compound 3-diazooxindole (**2a**) as the carbene precursor was conducted to screen the reaction conditions (Table 1). In the presence of a noble metal catalyst such as $Rh(OAc)_2$, $RhCl_3$, $Pd(PPh_3)_4$, $PdCl_2$, or $Pd(OAc)_2$, no reaction occurred at ambient temperature (see the Supporting Information for details). By means of a Lewis acid catalyst (10 mol%) of transition or main group metal, that is, $Cu(OTf)_2$, $Zn(OTf)_2$, $FeCl_3$, or $TiCl_4$, the 1:1.5 molar ratio reaction of **1a** and **2a** in dichloromethane gave a detectable amount of the target product 3-vinylated oxindole **3a** (6–32%) at

Table 1. Optimization of the reaction conditions.[a]



Entry	Catalyst	Solvent	Temp. (°C)	Yield[b] [%]
1	$Cu(OTf)_2$	CH_2Cl_2	25	6
2	$Zn(OTf)_2$	CH_2Cl_2	25	11
3	$FeCl_3$	CH_2Cl_2	25	30
4	$TiCl_4$	CH_2Cl_2	25	32
5		HFIP	25	N.D.
6[c]		HFIP	90	70
7	$Cu(OTf)_2$	HFIP	25	42
8	$Zn(OTf)_2$	HFIP	25	63
9	$FeCl_3$	HFIP	25	56
10	$TiCl_4$	HFIP	25	68
11	$B(C_6F_5)_3$	HFIP	25	83
12	$B(C_6F_5)_3$	CH_2Cl_2	25	8
13	$B(C_6F_5)_3$	toluene	25	6
14	$B(C_6F_5)_3$	*i*PrOH	25	N.D.
15[c]		*i*PrOH	90	N.D.
16[d]	$B(C_6F_5)_3$	HFIP	25	83 (80)[e]

[a] Conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), catalyst (10 mol%), solvent (2.0 mL), air, 18 h.
[b] Determined by ^{1}H NMR analysis by using 1,3,5-trimethoxybenzene as the internal standard.
[c] 36 h.
[d] **1a** (0.3 mmol), **2a** (0.45 mmol).
[e] Isolated yield given in parentheses.

ambient temperature under an air atmosphere (Table 1, entries 1–4). Compound **3a** was formally formed through carbene insertion into the α-alkenyl C–H bond of internal alkene **1a**. In the absence of a Lewis acid catalyst, the reaction did not proceed in either dichloromethane or HFIP at ambient temperature, whereas compound **3a** could be increasingly formed from the reaction in HFIP by elevating the reaction temperature, and thus 70% yield was reached at 90 °C by extending the reaction time to 36 hours (Table 1, entries 5 and 6; see the SI). In this case, HFIP might activate both the internal alkene **1a** and diazo compound **2a**. Using the same Cu(II), Zn(II), Fe(III), and Ti(IV) Lewis acid catalysts in HFIP at ambient temperature obviously enhanced the yield of **3a** to 42–68% (Table 1, entries 7–10). To our delight, further screening of non-metallic Lewis acids led to discovery of the most efficient catalyst, that is, large sterically hindered Lewis acid tris(pentafluorophenyl)borane ($B(C_6F_5)_3$), for the studied reaction, and **3a** was formed in 83% yield (Table 1, entry 11; see the SI). However, other boron Lewis acids such as BCl_3, BEt_3, and $B(OMe)_3$ only exhibited moderate to poor catalytic activity in HFIP (see the SI). It was

also noticed that $B(C_6F_5)_3$ behaved as a poor catalyst for the reaction of **1a** and **2a** in dichloromethane or toluene at ambient temperature. As a comparison to HFIP, $B(C_6F_5)_3$ exhibited no catalytic activity in isopropanol at ambient temperature or the elevated temperature (90 °C) (Table 1, entries 12–15). Under the optimal conditions, 80% isolated yield was obtained for **3a** (Table 1, entry 16). It is noteworthy that the molecular structure of **3a** was further confirmed by the X-ray single crystal structural determination with thermal ellipsoids at the 50% probability level (see Figure 1 and the SI for details).

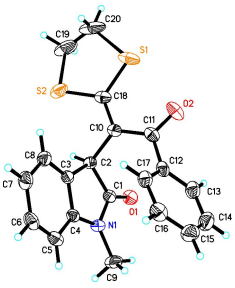
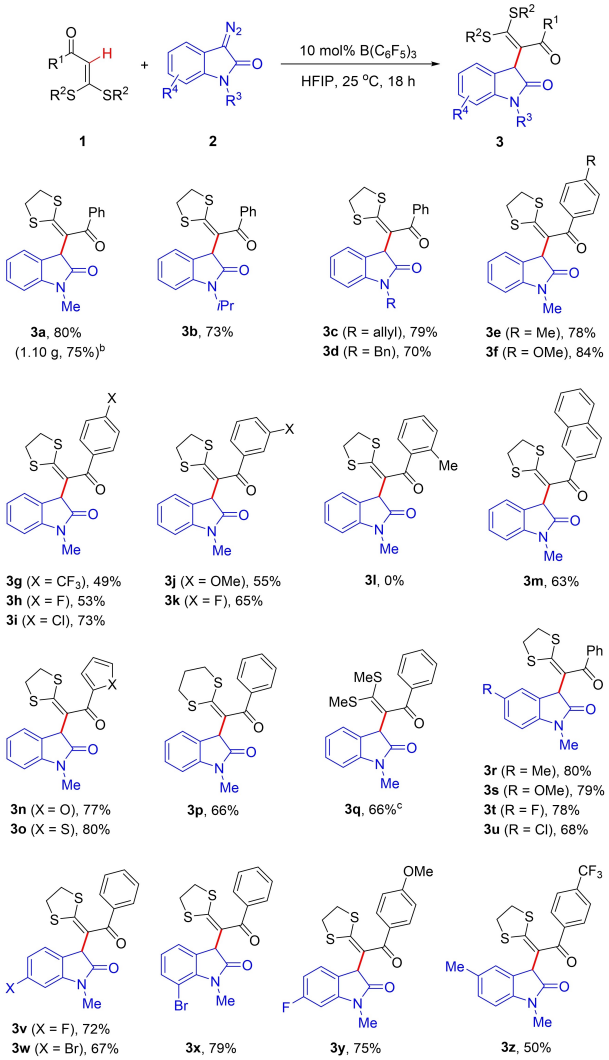


Figure 1. X-ray structure of **3a**.

Table 2. Scopes of α-oxo ketene dithioacetals (**1**) and 3-diazooxindoles (**2**).[a]



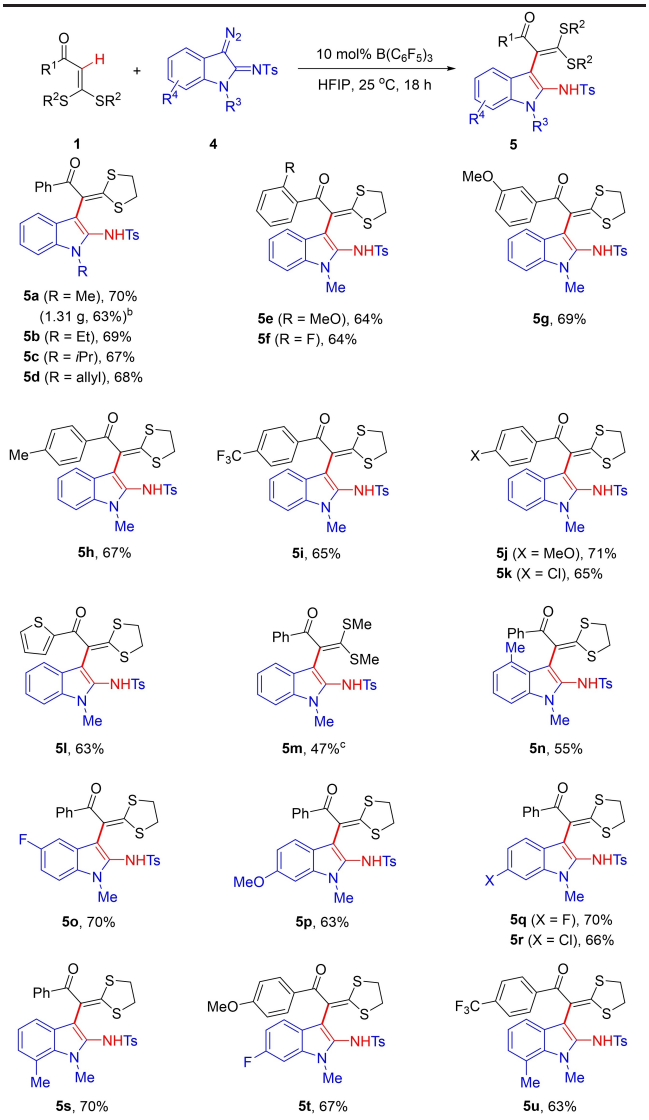
[a] Conditions: **1** (0.3 mmol), **2** (0.45 mmol), $B(C_6F_5)_3$ (0.03 mmol), HFIP (3 mL), 25 °C, 18 h, air, isolated yields.
[b] **1a** (4.0 mmol), **2a** (6.0 mmol).
[c] 59 °C.

Next, the scopes of α-oxo ketene dithioacetals (**1**) and 3-diazooxindoles (**2**) were explored (Table 2). To demonstrate the synthetic practicality, gram-scale synthesis of **3a** was performed in 75% isolated yield. The substituents on the nitrogen atom of the indolyl ring could be altered from methyl to isopropyl, allyl, and benzyl, resulting in the corresponding carbene insertion into C–H products **3b**–**3d** in 70–79% yields. Notably, *N*-unprotected and *N*-Boc (*tert*-butoxycarbo-nyl)-protected 3-diazooxindoles could not undergo the same type of reaction with **1a** under the stated conditions, which suggests that appropriate electron-donating capability of the *N*-heterocycle in 3-diazooxindoles (**2**) is required to render the desired carbene insertion into C–H process. Obvious electronic and steric effects were observed from the substituents on the aryl moieties of α-aroyl ketene dithioacetals (**1**). 4-Electron-donating groups such as methyl and methoxy promoted the reaction, while 4-electron-withdrawing groups such as trifluoromethyl, fluoro, and chloro groups diminished the reaction efficiency, leading to the target products **3e** (78%), **3f** (84%), and **3g**–**3i** (49–73%), respectively. 3-Positioned methoxy and fluoro groups exhibited an obvious steric effect on the formation of **3j** (55%) and **3k** (65%), whereas 2-methyl completely inhibited this reaction to generate **3l** (0%). Bulky 2-naphthyl-based dithioacetal **1m** also effectively reacted with diazo compound **2a** to afford product **3m** (63%). The reaction of 2-furanoyl and 2-thienoyl-supported ketene dithioacetals with **2a** efficiently proceeded to form the target products **3n** and **3o** (77–80%). Six-membered cyclic α-benzoyl ketene dithioacetal (**1p**) and open-chain α-benzoyl ketene di(methylthio)acetal (**1q**) showed lower reactivities than the five-membered cyclic α-benzoyl ketene dithioacetal (**1a**), and their reactions with **2a** gave products **3p** and **3q** in 66% yield. It is noteworthy that the temperature had to be elevated to 59 °C for the reaction of **1q** and **2a** to access **3q**. A remarkable steric effect was observed from 4-positioned methyl group on the benzo moiety of 3-diazooxindoles (**2**), which completely inhibited the desired carbene insertion into C–H reaction. 5-Chloro group on the benzo moiety showed an electronic effect on the formation of **3u** (68%) as compared with the impact from 5-methyl (**3r**, 80%), 5-methoxy (**3s**, 79%), and 5-fluoro (**3t**, 78%). 6-

Fluoro, 6-bromo, and 7-bromo-functionalized 3-diazooxindoles efficiently underwent the reaction with **1a** to produce the corresponding target products **3v**–**3x** (67–79%). By means of the present synthetic protocol, multisubstituted carbene insertion into C–H products **3y** (75%) and **3z** (50%) were synthesized, respectively.

The protocol generality was further investigated by using 3-diazoindolin-2-imines (**4**) as the carbene precursors under the same optimal conditions (Table 3). 3-Diazoindolin-2-imines have been well used as the practical building blocks for direct construction of indole substructures.[19] In our case, compounds **4** reacted with α-oxo ketene dithioacetals (**1**) formed the desired carbene insertion into alkenyl C–H products which then tautomerized to the corresponding indole derivatives **5**. The reaction of *N*-methyl, ethyl, isopropyl, and allyl-protected 3-diazoindolin-2-imines with **1a** gave products **5a**–**5d** in 67–70% yields. To demonstrate the synthetic practicality, gram-scale synthesis of **5a** was performed in a 63% isolated yield (1.31 g). However, *N*-unprotected 3-diazoindolin-2-imine (R=H) did not react at all under the same condition. It was found that 2-, 3-, and 4-positioned substituents, that is, methoxy, methyl, trifluoromethyl, fluoro, and chloro groups, on the aroyl moieties of α-oxo ketene dithioacetals (**1**) exhibited no obvious steric and electronic effects, leading to the corresponding products **5e**–**5k** in 63–71% yields. Notably, the molecular structure of compound **5i** was further verified by the X-ray single-crystal structural determination with thermal ellipsoids at the 50% probability level (Figure 2). 2-Thienyl-based α-oxo ketene dithioacetal also reacted well with **4a** to produce the target product **5l** (63%). The open-chain α-benzoyl ketene di(methylthio)acetal reacted less efficiently with **4a** than its cyclic analogs, and their reaction had to be conducted at an elevated temperature (59 °C) to generate compound **5m** in a moderate yield (47%). Unexpectedly, only a small steric effect was observed from 4-methyl on the benzo moiety of 3-diazoindolin-2-imine **4n** to render the formation of **5n** (55%), while such a 4-methyl in 3-diazooxindoles completely inhibited the desired carbene insertion into alkenyl C–H reaction. The 5-, 6-, and 7-substituents such as fluoro, methoxy, chloro, and methyl on the benzo moiety of **4** did not exhibit obvious steric and/or electronic effect on the reaction efficiency, and the target products **5o**–**5s** were obtained in 63–70% yields. Using this established synthetic protocol, multisubstituted indole derivatives **5t** (67%) and **5u** (63%) were synthesized, respectively. Other diazo compounds such as donor/donor-type diphenyldiazomethane, donor/acceptor-type ethyl phenyldiazo-acetate, and acceptor/acceptor-type diethyl diazomalonate were also tested in the reaction with **1a**, but no carbene insertion into alkenyl C–H

Table 3. Scopes of α-oxo ketene dithioacetals (**1**) and 3-diazoindolin-2-imines (**4**).[a]



[a] Conditions: **1** (0.3 mmol), **4** (0.45 mmol), $B(C_6F_5)_3$ (0.03 mmol), HFIP (3 mL), 25 °C, 18 h, air, isolated yields.
[b] **1a** (4.0 mmol), **4a** (6.0 mmol).
[c] 59 °C.

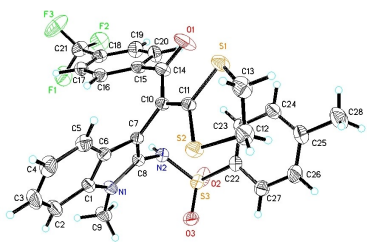
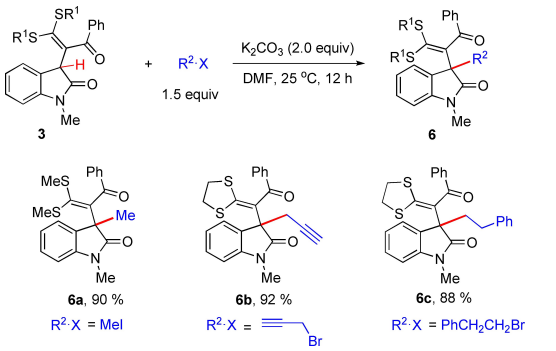
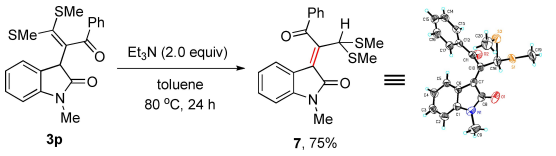


Figure 2. X-ray structure of **5i**.

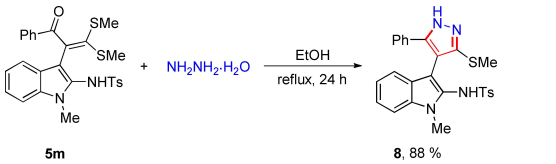
products were detected. These results have suggested that five-membered indolone and indolin-2-imine substructures in **2** and **4** may facilitate the studied carbene insertion into alkenyl C–H reaction.



(1)



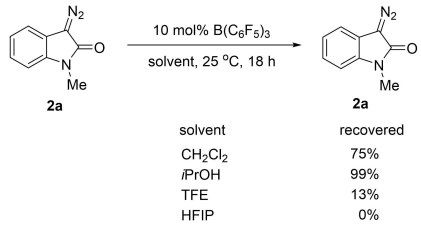
(2)



(3)

The potential applicability of the resultant 3-vinylated oxindole and indole derivatives was investigated. It was found that compounds **3** could not undergo tautomerization to form the corresponding 2-hydroxy-indole derivatives. However, in the presence of K_2CO_3, 3-vinylated oxindoles **3** efficiently reacted with haloalkanes to form 3-vinyl-3-alkyl oxindoles **6** (88–92%), building an all-carbon substituted quaternary carbon center [eq (1)]. Treatment of compound **3p** with triethylamine in toluene under heating afforded its tautomer **7** (75%) which was structurally confirmed by the X-ray single-crystal structural analysis [eq (2)]. Reacting compound **5m** with excessive hydrazine hydrate in refluxing ethanol gave bi(*N*-heteroaryl) indole-pyrazole compound **8** in 88% yield [eq (3)].

Control experiments were conducted to probe into the reaction mechanism (Scheme 2). With the aim to understand the role of HFIP in the studied carbene insertion reactions, diazo compound **2a** was treated with $B(C_6F_5)_3$ in dichloromethane, isopropanol, 2,2,2-trifluoroethanol (TFE), and HFIP at ambient temperature for 18 hours, respectively. It was found that both the fluorinated solvents 2,2,2-trifluoroethanol and HFIP facilitated the decomposition of **2a** under the stated conditions, and HFIP behaved most effectively



Scheme 2. Decomposition of diazo compound **2a** in the reaction media.

to enable complete decomposition of **2a** to form no identified products, while isopropanol was completely inactive. These experiments have revealed that diazo compound **2a** can be activated by HFIP as both the mediator and solvent through possible hydrogen bonding between **2a** and HFIP assisted by Lewis acid $B(C_6F_5)_3$. Addition of alkenyl C–H compound **1a** to the above pretreated mixture of **2a** and 10 mol% $B(C_6F_5)_3$ in HFIP did not lead to the target product **3a**, suggesting that no stable carbene intermediate withstands the reaction conditions.

The possible interaction between Lewis acid $B(C_6F_5)_3$ and HFIP was investigated by NMR analysis. In $CDCl_3$, HFIP exhibited its proton resonances at 4.40 ppm as a multiplet and at 3.04 ppm as a doublet. In the presence of $B(C_6F_5)_3$, the corresponding proton resonance signal of the hydroxyl group in HFIP was shifted downfield to 3.56 ppm from 3.04 ppm (Figure 3). It was also observed that in the presence of $B(C_6F_5)_3$, the corresponding fluorine resonance signal of the trifluoromethyl group in HFIP was partially shifted downfield from −75.8 ppm to −74.8 ppm and

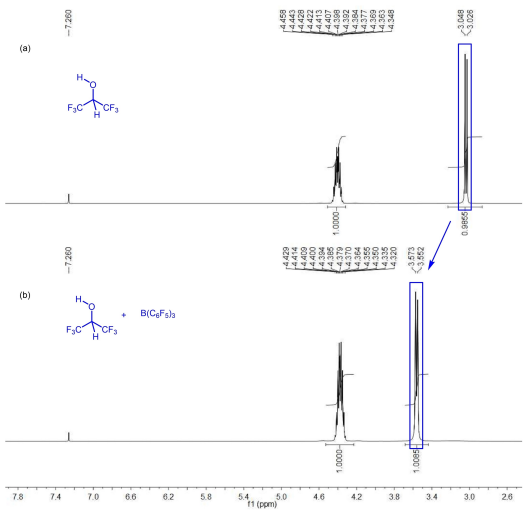
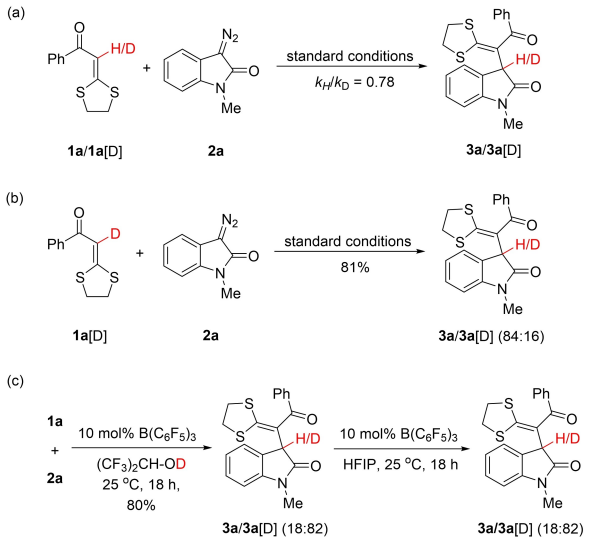


Figure 3. Interaction of $B(C_6F_5)_3$ and HFIP by proton NMR analysis. Conditions:[a] ^{1}H NMR spectrum of HFIP (1 M) in $CDCl_3$.[b] ^{1}H NMR spectrum of $B(C_6F_5)_3$ (0.2 M) with HFIP (1 M) in $CDCl_3$.

−75.1 ppm, and the *meta* and *para* ^{19}F signals of $B(C_6F_5)_3$ were shifted upfield about 0.3 ppm and 1.1 ppm, respectively, with their gap reduced by about 0.8 ppm (SI, Figures S3–S5). These results suggest a strong interaction between $B(C_6F_5)_3$ and HFIP in solution presumably through coordination of the hydroxyl oxygen atom of HFIP to the boron atom in $B(C_6F_5)_3$. The activated hydroxyl of HFIP may form a strong hydrogen bond (B···O–H···O=C or B···O–H···N=C) with the diazo substrates, thus activating **2** or **4** to undergo the desired carbene insertion into alkenyl C–H reaction. The adduct of $B(C_6F_5)_3$ and HFIP was not successfully synthesized by stirring a mixture of $B(C_6F_5)_3$ and HFIP under the reaction conditions, and then work-up by evaporation of all the volatiles under reduced pressure. Such manipulations only recovered $B(C_6F_5)_3$, which suggests that adduct of $B(C_6F_5)_3$ and HFIP is not stable under the stated conditions.

The possible interactions between $B(C_6F_5)_3$ and diazooxindole **2a** and internal alkene **1a** in solution were also investigated by the ^{19}F NMR analysis (SI, Figures S4, S8, and S13). The three sets of ^{19}F NMR signals of $B(C_6F_5)_3$ in the presence of diazooxindole **2a** were upfield about 2.1–8.6 ppm, and those of $B(C_6F_5)_3$ in the presence of internal alkene **1a** were upfield about 2.3–3.0 ppm, respectively, which suggests a stronger interaction between $B(C_6F_5)_3$ and diazooxindole **2a** than that between $B(C_6F_5)_3$ and internal alkene **1a**. The ^{13}C NMR signal of the carbonyl of **2a** in the presence of $B(C_6F_5)_3$ was shifted downfield from 166.9 ppm to 173.5 ppm (SI, Figures S7 and S10), revealing an electron-withdrawing interaction between the carbonyl oxygen and Lewis acidic boron atoms presumably through weak coordination (C=O···B). In a similar interaction manner, the ^{13}C NMR signal of the carbonyl of **1a** in the presence of $B(C_6F_5)_3$ was partially shifted downfield from 185.7 ppm to 195.3 ppm (SI, Figures S12 and S15). Additionally, obvious chemical shifts were observed in the proton NMR spectra of the mixtures of **2a** and $B(C_6F_5)_3$, and **1a** and $B(C_6F_5)_3$ in solution, respectively (SI, Figures S9 and S14). These results have demonstrated the possible activation of substrates **1** and **2** by $B(C_6F_5)_3$ during the reaction.

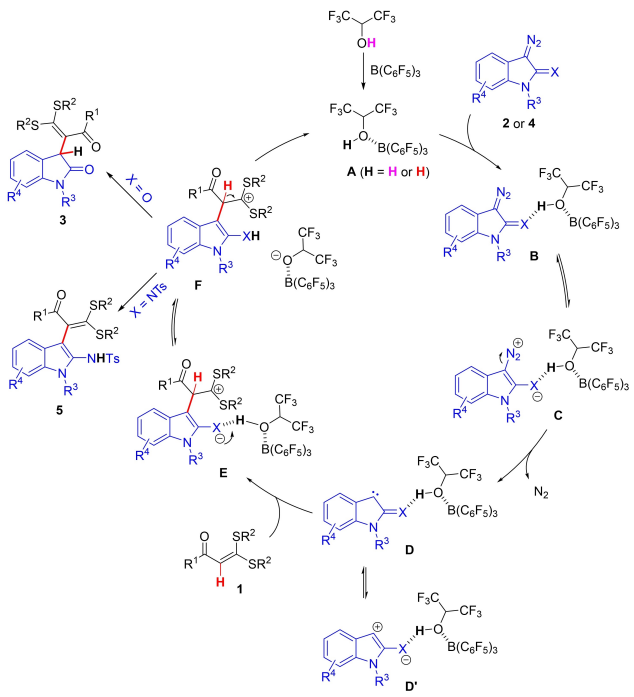
The kinetic isotope effect (KIE) was measured as shown in Scheme 3, and a value of $k_H/k_D = 0.78$ was obtained from the two parallel reactions of **1a** and its deuterated form **1a**[D] with **2a** under the standard conditions (Scheme 3a; see the SI for details). This inverse secondary deuterium kinetic isotope effect reveals that the alkenyl C–H cleavage was not involved in the rate-limiting step of the overall catalytic cycle.[20] As shown in Scheme 3b deuterated **1a**[D] reacted with **2a** to form a mixture of **3a** and **3a**[D] (84:16) in 81% yield, revealing that hydrogen of the newly formed C(sp^3)–H bond in **3a** is



Scheme 3. KIE and H/D exchange experiments.

originated from HFIP mediator and solvent, while deuterium in **3a**[D] came from the formal alkenyl C(sp^2)–D cleavage of **1a**[D]. The hydrogen origin in the newly formed C(sp^3)–H bond of **3** was further verified by conducting the reaction of **1a** and **2a** in hydroxyl-deuterated HFIP-OD under the standard conditions (Scheme 3c). Thus, a mixture of **3a** and **3a**[D] (18:82) was obtained in 80% yield, revealing the same hydrogen origin for the newly formed C(sp^3)–H bond of **3**. The mixture of **3a** and **3a**[D] (18:82) remained unchanged by further treatment with 10 mol% $B(C_6F_5)_3$ under the standard reaction conditions, suggesting no H–D exchange occurred for **3** under the stated conditions.

Based on the control and KIE experiments, a plausible mechanism is proposed in Scheme 4. Upon the addition of $B(C_6F_5)_3$ to HFIP solvent, adduct **A** is initially generated through coordination of the hydroxyl oxygen atom of HFIP to the boron atom of Lewis acid $B(C_6F_5)_3$. The activated hydroxyl then establishes a strong hydrogen bond (C=X···H–O···B, X=O or NTs) with the diazo compound (**2** or **4**), forming species **B** and **C**. Extrusion of dinitrogen results in carbene (**D**)/carbenium (**D′**) species which undergo carbene insertion into or electrophilic attack of carbenium ion at the alkenyl C–H bond of internal alkene **1**, forming species **E** and/or **F**. Regeneration of species **A** with a tautomerization produces 3-vinylated oxindole **3** (X=O), or directly gives 2-amino-3-vinylated indole **5** (X=NTs). It is noteworthy that the alkenyl C–H hydrogen is gradually incorporated to HFIP as the carbene insertion reaction proceeds. Because HFIP is also used as the solvent which is more excessive than the *in situ* generated alkenyl C–H hydrogen-incorporated HFIP, the majority of hydrogen in the newly formed C(sp^3)–H bond of **3** or



Scheme 4. Proposed mechanism.

5 is statistically originated from the mediator and solvent HFIP. However, based on the above-mentioned possible interactions of the substrates and Lewis acid $B(C_6F_5)_3$ the reaction pathway[5c,21] involving activation of the diazo compounds by $B(C_6F_5)_3$ for this carbene insertion into alkenyl C–H bonds cannot be excluded (see the SI for details).

Conclusions

In summary, HFIP mediated carbene insertion into internal alkenyl C–H bonds was successfully achieved in the presence of $B(C_6F_5)_3$ by means of indoline-based diazo compounds as the carbene precursors. A cooperative interaction of HFIP and $B(C_6F_5)_3$ enables such transformations to access 3-vinylated oxindole and indole derivatives. The present synthetic protocol features mild metal-free conditions, air atmosphere, diverse functional group tolerance, and 47–84% yields, offering an alternative route to carbene insertion into C–H bonds under metal-free and mild conditions.

Experimental Section

General Considerations

^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a 400 MHz spectrometer and all chemical shift values refer to $CDCl_3$ (δ(^{1}H), 7.26 ppm and δ(^{13}C), 77.16 ppm). X-Ray crystallographic analysis was achieved by the Analysis Center, Dalian Institute of Chemical Physics, Chinese Academy of Sciences. The HRMS analysis was obtained by ESI on a GC-TOF mass spectrometer. Column chromatographic purifications were performed on silica gel. All the chemical reagents were purchased from commercial sources and used as received unless otherwise indicated.

CCDC 2079793 (**3a**), 2159421 (**5i**), and 2159422 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/structures.

Indolin-2-one 3a; Typical Procedure for the Synthesis of Compounds 3 and 5

A mixture of **1a** (67 mg, 0.3 mmol), **2a** (78 mg, 0.45 mmol), and $B(C_6F_5)_3$ (15 mg, 0.03 mmol) in 3 mL HFIP was vigorously stirred at 25 °C for 18 h under an air atmosphere. After cooling to ambient temperature, all the volatiles were evaporated under reduced pressure. The resultant residue was purified by column chromatography on silica gel (eluent: petroleum ether (60–90 °C)/ethyl acetate = 10:1, v/v) to afford compound **3a** (88 mg, 80%).

3-(1-(1,3-Dithiolan-2-ylidene)-2-oxo-2-phenylethyl)-1-methylindolin-2-one (3a): 89 mg, 80% yield, yellow solid, m.p.: 191–192 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63–7.10 (m, 7H), 6.99 (t, J = 7.5 Hz, 1H), 6.66 (s, 1H), 4.89 (s, 1H), 3.36 (s, 4H), 3.04 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 193.2, 174.9, 166.8, 144.0, 139.4, 130.5, 128.2, 127.9, 127.6, 123.8, 122.5, 119.7, 108.0, 51.4, 39.1, 36.7, 26.3. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{20}H_{18}NO_2S_2$: 368.0779; found: 368.0769.

3-(1-(1,3-Dithiolan-2-ylidene)-2-oxo-2-phenylethyl)-1-isopropylindolin-2-one (3b): 87 mg, 73% yield, yellow solid, m.p.: 177–178 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98–6.98 (m, 7H), 6.96–6.68 (m, 2H), 4.80 (s, 1H), 4.51 (s, 1H), 3.22 (s, 4H), 1.33 (d, J = 5.3 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 193.0, 174.1, 166.4, 142.6, 139.4, 130.7, 128.2, 127.8, 123.9, 121.8, 119.7, 109.6, 51.4, 43.8, 38.9, 36.8, 19.3, 18.9. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{22}H_{22}NO_2S_2$: 396.1092; found: 396.1095.

3-(1-(1,3-Dithiolan-2-ylidene)-2-oxo-2-phenylethyl)-1-allylindolin-2-one (3c): 93 mg, 79% yield, yellow solid, m.p.: 195–196 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04–7.03 (m, 7H), 6.91 (t, J = 7.5 Hz, 1H), 6.64 (s, 1H), 5.67 (s, 1H), 5.15 (dd, J = 33.7, 13.7 Hz, 2H), 4.87 (s, 1H), 4.51–3.68 (m, 2H), 3.27 (s, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 193.2, 174.5, 166.5, 143.3, 139.4, 131.6, 130.7, 128.1, 127.7, 127.4, 123.8, 122.4, 119.7, 117.8, 108.9, 51.4, 42.7, 39.1, 36.8. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{22}H_{20}NO_2S_2$: 394.0935; found: 394.0934.

3-(1-(1,3-Dithiolan-2-ylidene)-2-oxo-2-phenylethyl)-1-benzylindolin-2-one (3d): 93 mg, 70% yield, white solid, m.p.: 93–94 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88–6.97 (m, 12H), 6.88 (t, J = 7.5 Hz, 1H), 6.56 (s, 1H), 5.11–4.77 (m, 2H), 4.51 (s, 1H), 3.54–2.82 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 193.2, 175.1, 143.4, 139.4, 135.9, 130.8, 128.7, 128.2, 127.9, 127.8, 127.6, 123.94, 122.6, 119.7, 109.1, 51.5, 44.3,

39.1, 36.8. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{26}H_{22}NO_2S_2$: 444.1092; found: 444.1085.

3-(1-(1,3-Dithiolan-2-ylidene)-2-oxo-2-(p–tolyl)ethyl)-1-methylindolin-2-one (3e): 89 mg, 78% yield, yellow solid, m.p.: 188–189 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (s, 2H), 7.25–7.14 (m, 2H), 7.08 (s, 2H), 6.98 (t, J=7.4 Hz, 1H), 6.70 (s, 1H), 4.90 (s, 1H), 3.32 (s, 4H), 3.09 (s, 3H), 2.30 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 193.1, 174.8, 165.3, 144.0, 141.1, 136.4, 128.6, 128.1, 127.9, 127.5, 123.7, 122.4, 119.9, 107.9, 51.4, 38.9, 36.7, 26.2, 21.4. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{21}H_{20}NO_2S_2$: 382.0935; found: 382.0954.

3-(1-(1,3-Dithiolan-2-ylidene)-2-(4-methoxyphenyl)-2-oxoethyl)-1-methylindolin-2-one (3f): 100 mg, 84% yield, yellow solid, m.p.: 185–186 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (s, 2H), 7.30–7.15 (m, 2H), 7.00 (t, J=7.5 Hz, 1H), 6.81 (d, J=7.1 Hz, 2H), 6.74 (d, J=7.3 Hz, 1H), 4.92 (s, 1H), 3.79 (s, 3H), 3.33 (s, 4H), 3.15 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 192.6, 175.0, 162.0, 144.1, 131.5, 130.4, 128.2, 127.6, 123.8, 122.5, 120.4, 113.4, 108.0, 55.4, 51.6, 39.0, 36.9, 26.4. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{21}H_{20}NO_3S_2$: 398.0885; found: 398.0893.

3-(1-(1,3-Dithiolan-2-ylidene)-2-oxo-2-(4-(trifluoro-methyl)phenyl)ethyl)-1-methylindolin-2-one (3g): 64 mg, 49% yield, yellow solid, m.p.: 187–188 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25–7.01 (m, 6H), 6.94 (t, J=7.5 Hz, 1H), 6.51 (s, 1H), 4.77 (s, 1H), 3.38 (s, 4H), 2.83 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 191.8, 174.8, 169.6, 143.9, 143.0, 131.7, 128.6, 127.7, 125.1, 124.6, 123.9, 122.7, 122.4, 119.7, 119.0, 108.1, 51.4, 39.4, 36.7, 26.2. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ −63.0. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{21}H_{17}F_3NO_2S_2$: 436.0653; found: 436.0649.

3-(1-(1,3-Dithiolan-2-ylidene)-2-(4-fluorophenyl)-2-oxoethyl)-1-methylindolin-2-one (3h): 61 mg, 53% yield, white solid, m.p.: 178–179 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (s, 2H), 7.22 (t, J=7.7 Hz, 1H), 7.16 (d, J=7.1 Hz, 1H), 6.98 (t, J=7.5 Hz, 1H), 6.91 (s, 2H), 6.69 (s, 1H), 4.86 (s, 1H), 3.37 (s, 4H), 3.07 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 192.0, 174.9, 166.7, 164.1 (d, J_{C-F}=251.2 Hz), 144.0, 135.5, 130.2 (d, J_{C-F}=6.7 Hz), 128.4, 127.5 (d, J_{C-F}=6.2 Hz), 123.8, 122.6, 119.6, 114.9 (d, J_{C-F}=21.1 Hz), 108.1, 51.4, 39.1, 36.8, 26.3. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ −108.7. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{20}H_{17}FNO_2S_2$: 386.0685; found: 386.0685.

3-(2-(4-Chlorophenyl)-1-(1,3-dithiolan-2-ylidene)-2-oxoethyl)-1-methylindolin-2-one (3i): 88 mg, 73% yield, yellow solid, m.p.: 200–201 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75–7.06 (m, 6H), 6.99 (t, J=7.5 Hz, 1H), 6.69 (s, 1H), 4.86 (s, 1H), 3.38 (s, 4H), 3.06 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 192.0, 174.8, 167.5, 144.0, 137.8, 136.6, 129.2, 128.4, 128.1, 127.4, 123.8, 122.6, 119.4, 108.1, 51.4, 39.2, 36.8, 26.3. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{20}H_{17}ClNO_2S_2$: 402.0389; found: 402.0386.

3-(1-(1,3-Dithiolan-2-ylidene)-2-(3-methoxyphenyl)-2-oxoethyl)-1-methylindolin-2-one (3j): 66 mg, 55% yield, yellow solid, m.p.: 130–131 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48–7.05 (m, 4H), 6.98 (t, J=7.5 Hz, 1H), 6.87 (s, 2H), 6.66 (s, 1H), 4.91 (s, 1H), 3.70 (s, 3H), 3.36 (s, 4H), 3.07 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 192.9, 174.9, 167.1, 159.1, 144.0, 140.6, 129.0, 128.2, 127.5, 123.8, 122.4, 119.9, 119.5, 117.4, 111.6, 108.0, 55.3, 51.4, 39.0, 36.7, 26.3. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{21}H_{20}NO_3S_2$: 398.0885; found: 398.0895.

3-(1-(1,3-Dithiolan-2-ylidene)-2-(3-fluorophenyl)-2-oxoethyl)-1-methylindolin-2-one (3k): 75 mg, 65% yield, yellow solid, m.p.: 125–126 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84–7.05 (m, 4H), 7.04–6.80 (m, 3H), 6.63 (s, 1H), 4.82 (s, 1H), 3.35 (s, 4H), 3.01 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 191.2, 174.6, 168.4, 161.88 (d, J_{C-F}=247.7 Hz), 143.8, 141.41 (d, J_{C-F}=6.2 Hz), 129.4, 128.2, 127.2, 123.6, 123.1, 122.4, 118.9, 117.16 (d, J_{C-F}=19.4 Hz), 114.32 (d, J_{C-F}=21.1 Hz), 107.9, 51.1, 39.0, 36.6, 26.1. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ −112.3. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{20}H_{17}FNO_2S_2$: 386.0685; found: 386.0694.

3-(1-(1,3-Dithiolan-2-ylidene)-2-(naphthalen-2-yl)-2-oxoethyl)-1-methylindolin-2-one (3m): 80 mg, 63% yield, yellow solid, m.p.: 140–141 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29–7.57 (m, 5H), 7.56–7.37 (m, 3H), 7.20 (t, J=7.3 Hz, 1H), 7.03 (t, J=7.4 Hz, 1H), 6.49 (s, 1H), 4.93 (s, 1H), 3.39 (s, 4H), 2.77 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 193.2, 174.9, 166.8, 143.9, 136.6, 134.1, 131.9, 128.9, 128.3, 127.9, 127.6, 127.4, 126.3, 124.8, 123.9, 122.5, 120.1, 108.0, 51.7, 39.2, 36.6, 26.1. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{24}H_{20}NO_2S_2$: 418.0935; found: 418.0933.

3-(1-(1,3-Dithiolan-2-ylidene)-2-(furan-2-yl)-2-oxoethyl)-1-methylindolin-2-one (3n): 82 mg, 77% yield, yellow solid, m.p.: 172–173 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (s, 1H), 7.30 (dd, J=11.9, 4.4 Hz, 1H), 7.22 (d, J=7.1 Hz, 2H), 7.03 (t, J=7.2 Hz, 1H), 6.86 (d, J=7.6 Hz, 1H), 6.44 (s, 1H), 5.34 (s, 1H), 3.28 (s, 7H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 178.4, 175.1, 168.0, 152.5, 145.1, 144.3, 128.2, 127.3, 124.1, 122.6, 118.1, 117.7, 112.1, 107.9, 50.4, 38.2, 36.9, 26.6. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{18}H_{16}NO_3S_2$: 358.0572; found: 358.0572.

3-(1-(1,3-Dithiolan-2-ylidene)-2-oxo-2-(thiophen-2-yl)-ethyl)-1-methylindolin-2-one (3o): 89 mg, 80% yield, yellow solid, m.p.: 179–180 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.53 (d, J=4.8 Hz, 1H), 7.29 (t, J=7.7 Hz, 1H), 7.21 (d, J=7.3 Hz, 1H), 7.04 (d, J=7.5 Hz, 1H), 7.02–6.94 (m, 1H), 6.82 (d, J=7.7 Hz, 1H), 5.18 (s, 1H), 3.30 (s, 4H), 3.23 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 184.5, 174.7, 165.4, 144.1, 143.3, 132.2, 131.1, 128.3, 127.3, 127.1, 124.0, 122.6, 119.2, 108.1, 51.0, 38.4, 37.0, 26.5. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{18}H_{16}NO_2S_3$: 374.0343; found: 374.0344.

3-(1-(1,3-Dithian-2-ylidene)-2-oxo-2-phenylethyl)-1-methylindolin-2-one (3p): 76 mg, 66% yield, yellow solid, m.p.: 135–137 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (s, 2H), 7.29 (t, J=6.9 Hz, 1H), 7.23–7.02 (m, 4H), 6.90 (t, J=7.4 Hz, 1H), 6.52 (d, J=7.0 Hz, 1H), 4.91 (s, 1H), 3.23–2.83 (m, 6H), 2.83–2.70 (m, 1H), 2.28–2.01 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 194.1, 175.3, 153.6, 144.2, 139.2, 131.7, 130.1, 128.4, 128.2, 128.0, 127.9, 124.0, 122.5, 108.0, 49.7, 29.5, 29.3, 26.4, 24.0. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{21}H_{20}NO_2S_2$: 382.0935; found: 382.0938.

3-(1,1-Bis(methylthio)-3-oxo-3-phenylprop-1-en-2-yl)-1-methylindolin-2-one (3q): 93 mg, 66% yield, yellow solid, m.p.: 181–182 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 2H), 7.54–7.31 (m, 3H), 7.31–7.08 (m, 2H), 6.96 (t, J=7.2 Hz, 1H), 6.71 (d, J=7.2 Hz, 1H), 5.05 (s, 1H), 3.13 (s, 3H), 2.29 (s, 3H), 2.10 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 195.0, 174.2, 144.2, 143.5, 140.8, 137.2, 132.8, 128.9, 128.3, 128.2, 126.7, 124.2, 122.3, 107.9, 50.8, 26.4, 17.2, 16.8. HRMS (ESI-TOF) m/z: [M+H]$^+$ calcd for $C_{20}H_{20}NO_2S_2$: 370.0935; found: 370.0943.

3-(1-(1,3-Dithiolan-2-ylidene)-2-oxo-2-phenylethyl)-1,5-dimethylindolin-2-one (3r): 92 mg, 80% yield, yellow solid, m.p.: 196–197 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17–7.07 (m, 5H), 7.07–6.87 (m, 2H), 6.55 (s, 1H), 4.87 (s, 1H), 3.35 (s, 4H), 3.02 (s, 3H), 2.28 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 193.2, 174.8, 166.7, 141.6, 139.4, 132.0, 130.5, 128.4, 127.9, 127.6, 124.6, 119.8, 107.7, 51.4, 39.0, 36.7, 26.3, 21.1. HRMS (ESI-TOF) m/z: [M+H]$^+$ calcd for $C_{21}H_{20}NO_2S_2$: 382.0935; found: 382.0936.

3-(1-(1,3-Dithiolan-2-ylidene)-2-oxo-2-phenylethyl)-5-methoxy-1-methylindolin-2-one (3s): 93 mg, 79% yield, yellow solid, m.p.: 197–198 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44–6.94 (m, 5H), 6.93–6.68 (m, 2H), 6.57 (s, 1H), 4.89 (s, 1H), 3.75 (s, 3H), 3.37 (s, 4H), 3.03 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 193.3, 174.6, 166.9, 156.1, 139.5, 137.7, 130.6, 128.9, 128.0, 127.8, 119.7, 112.7, 111.1, 108.3, 55.9, 51.9, 39.0, 36.8, 26.4. HRMS (ESI-TOF) m/z: [M+H]$^+$ calcd for $C_{21}H_{20}NO_3S_2$: 398.0885; found: 398.0886.

3-(1-(1,3-Dithiolan-2-ylidene)-2-oxo-2-phenylethyl)-5-fluoro-1-methylindolin-2-one (3t): 90 mg, 78% yield, yellow solid, m.p.: 217–218 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91–7.09 (m, 5H), 7.08–6.79 (m, 2H), 6.58 (s, 1H), 4.88 (s, 1H), 3.38 (s, 4H), 3.05 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 193.2, 174.7, 167.0, 159.3 (d, J_{C-F}=240.6 Hz), 140.2, 139.4, 130.8, 129.2, 128.1, 127.8, 119.4 114.4 (d, J_{C-F}=23.6 Hz), 112.0 (d, J_{C-F}=24.9 Hz), 108.4 (d, J_{C-F}=8.1 Hz), 51.8, 39.3, 36.8, 26.5. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ −118.1. HRMS (ESI-TOF) m/z: [M+H]$^+$ calcd for $C_{20}H_{17}FNO_2S_2$: 386.0685; found: 386.0686.

3-(1-(1,3-Dithiolan-2-ylidene)-2-oxo-2-phenylethyl)-5-chloro-1-methylindolin-2-one (3u): 82 mg, 68% yield, white solid, m.p.: 220–221 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04–7.22 (m, 5H), 7.22–7.08 (m, 2H), 6.59 (s, 1H), 4.89 (s, 1H), 3.40 (s, 4H), 3.06 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 193.1, 174.6, 167.0, 142.8, 139.4, 130.8, 129.4, 128.2, 128.0, 127.8, 124.3, 119.4, 108.9, 51.5, 39.4, 36.8, 26.5. HRMS (ESI-TOF) m/z: [M+H]$^+$ calcd for $C_{20}H_{17}ClNO_2S_2$: 402.0389; found: 402.0381.

3-(1-(1,3-Dithiolan-2-ylidene)-2-oxo-2-phenylethyl)-6-fluoro-1-methylindolin-2-one (3v): 83 mg, 72% yield, yellow solid, m.p.: 153–154 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81–7.17 (m, 5H), 7.14–6.98 (m, 1H), 6.80–6.54 (m, 1H), 6.39 (s, 1H), 4.83 (s, 1H), 3.36 (s, 4H), 3.02 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 193.2, 175.4, 166.7, 163.14 (d, J_{C-F}=244.9 Hz), 145.51 (d, J_{C-F}=11.7 Hz), 139.3, 130.6, 128.0, 127.6, 124.71 (d, J_{C-F}=9.7 Hz), 122.8, 119.5, 108.46 (d, J_{C-F}=22.3 Hz), 96.84 (d, J_{C-F}=27.6 Hz), 51.0, 39.2, 36.7, 26.4. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ −111.9. HRMS (ESI-TOF) m/z: [M+H]$^+$ calcd for $C_{20}H_{17}FNO_2S_2$: 386.0685; found: 386.0682.

3-(1-(1,3-Dithiolan-2-ylidene)-2-oxo-2-phenylethyl)-6-bromo-1-methylindolin-2-one (3w): 89 mg, 67% yield, yellow solid, m.p.: 160–162 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72–7.14 (m, 5H), 7.09 (d, J=7.8 Hz, 1H), 7.01 (d, J=7.5 Hz, 1H), 6.78 (s, 1H), 4.78 (s, 1H), 3.34 (s, 4H), 3.01 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 193.0, 174.7, 166.9, 145.3, 139.2, 130.7, 127.9, 127.6, 126.4, 125.1, 124.9, 121.6, 119.2, 111.4, 51.0, 39.2, 36.7, 26.4. HRMS (ESI-TOF) m/z: [M+H]$^+$ calcd for $C_{20}H_{17}BrNO_2S_2$: 445.9884; found: 445.9878.

3-(1-(1,3-Dithiolan-2-ylidene)-2-oxo-2-phenylethyl)-7-bromo-1-methylindolin-2-one (3x): 106 mg, 79% yield, yellow solid, m.p.: 173–174 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77–7.33 (m, 2H), 7.33–7.14 (m, 4H), 7.08 (d, J=6.4 Hz, 1H), 6.81 (t, J=7.7 Hz, 1H), 4.86 (s, 1H), 3.38 (s, 7H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 193.1, 175.3, 167.1, 141.3, 139.2, 133.8, 130.7, 128.0, 127.6, 123.6, 122.9, 119.6, 102.4, 51.4, 39.3, 36.8, 30.0. HRMS (ESI-TOF) m/z: [M+H]$^+$ calcd for $C_{20}H_{17}BrNO_2S_2$: 445.9884; found: 445.9889.

3-(1-(1,3-Dithiolan-2-ylidene)-2-(4-methoxyphenyl)-2-oxoethyl)-6-fluoro-1-methylindolin-2-one (3y): 93 mg, 75% yield, yellow solid, m.p.: 191–192 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (s, 2H), 7.20–7.05 (m, 1H), 6.82 (d, J=8.0 Hz, 2H), 6.72–6.60 (m, 1H), 6.47 (d, J=8.3 Hz, 1H), 4.85 (s, 1H), 3.80 (s, 3H), 3.34 (s, 4H), 3.13 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 192.7, 175.6, 163.2 (d, J_{C-F}=244.8 Hz), 162.3, 145.7 (d, J_{C-F}=11.6 Hz), 131.4, 130.5, 124.8 (d, J_{C-F}=9.7 Hz), 122.9, 120.3, 113.5, 108.6 (d, J_{C-F}=22.4 Hz), 96.9 (d, J_{C-F}=27.6 Hz), 55.5, 51.2, 39.2, 37.0, 26.6. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ −112.1. HRMS (ESI-TOF) m/z: [M+H]$^+$ calcd for $C_{21}H_{19}FNO_3S_2$: 416.0790; found: 416.0780.

3-(1-(1,3-Dithiolan-2-ylidene)-2-oxo-2-(4-(trifluoro-methyl)phenyl)ethyl)-1,5-dimethyl-indolin-2-one (3z): 67 mg, 50% yield, yellow solid, m.p.: 178–179 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45–6.81 (m, 6H), 6.44 (s, 1H), 4.81 (s, 1H), 3.66–2.65 (m, 7H), 2.30 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 191.8, 174.6, 169.6, 143.0, 141.5, 132.4, 128.8, 127.7, 125.1, 124.7, 124.4, 122.4, 119.7, 119.2, 107.9, 51.6, 39.4, 36.6, 26.2, 21.2. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ −63.0. HRMS (ESI-TOF) m/z: [M+H]$^+$ calcd for $C_{22}H_{19}F_3NO_2S_2$: 450.0809; found: 450.0826.

***N*-(3-(1-(1,3-Dithiolan-2-ylidene)-2-oxo-2-phenyl-ethyl)-1-methyl-1H-indol-2-yl)-4-methyl-benzene-sulfonamide (5a)**: 110 mg, 70% yield, yellow solid, m.p.: 122–123 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J=8.3 Hz, 2H), 7.25 (t, J=7.8 Hz, 2H), 7.23–7.17 (m, 2H), 7.13–7.06 (m, 4H), 7.06–6.97 (m, 3H), 5.66 (s, 1H), 3.65 (s, 3H), 3.31 (dd, J=7.5, 5.4 Hz, 2H), 3.16 (dt, J=10.4, 5.1 Hz, 1H), 2.95 (dt, J=11.3, 7.9 Hz, 1H), 2.28 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 188.7, 168.9, 143.7, 139.0, 136.7, 135.2, 131.1, 129.8, 128.2, 127.9, 127.1, 126.7, 123.8, 123.2, 121.4, 120.0, 116.0, 111.6, 110.3, 39.8, 35.6, 29.8, 21.8. HRMS (ESI-TOF) m/z: [M+H]$^+$ calcd for $C_{27}H_{25}N_2O_3S_3$: 521.1027; found: 521.1023.

***N*-(3-(1-(1,3-Dithiolan-2-ylidene)-2-oxo-2-phenyl-ethyl)-1-ethyl-1H-indol-2-yl)-4-methyl-benzene-sulfonamide (5b)**: 74 mg, 69% yield, yellow solid, m.p.: 110–111 °C. ^{1}H NMR

(400 MHz, $CDCl_3$) δ 7.59 (d, J=8.0 Hz, 2H), 7.39 (d, J=8.2 Hz, 2H), 7.30 (t, J=7.2 Hz, 2H), 7.24–7.16 (m, 4H), 7.16–7.05 (m, 3H), 5.49 (s, 1H), 4.46–4.30 (m, 1H), 4.30–4.14 (m, 1H), 3.37 (t, J=12.5 Hz, 2H), 3.23 (dd, J=11.0, 4.9 Hz, 1H), 2.99 (dd, J=18.5, 8.7 Hz, 1H), 2.39 (s, 3H), 1.17 (t, J=7.0 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 188.3, 169.5, 143.6, 139.1, 136.6, 134.0, 130.9, 129.7, 127.9, 127.0, 126.1, 124.1, 123.1, 121.6, 119.8, 115.8, 111.9, 110.5, 39.8, 37.7, 35.6, 21.8, 15.0. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{28}H_{27}N_2O_3S_3$: 535.1184; found: 535.1189.

***N*-(3-(1-(1,3-Dithiolan-2-ylidene)-2-oxo-2-phenyl-ethyl)-1-isopropyl-1H-indol-2-yl)-4-methylbenzene-sulfonamide (5c)**: 110 mg, 67% yield, yellow solid, m.p.: 132–133 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J=8.4 Hz, 1H), 7.58 (d, J=7.9 Hz, 2H), 7.43 (d, J=7.9 Hz, 1H), 7.32 (d, J=6.8 Hz, 1H), 7.26 (d, J=8.0 Hz, 1H), 7.21 (d, J=8.0 Hz, 2H), 7.19–7.09 (m, 5H), 5.38 (s, 1H), 5.02–4.85 (m, 1H), 3.39 (dd, J=7.8, 4.8 Hz, 2H), 3.28–3.18 (m, 1H), 2.98 (dd, J=19.3, 8.4 Hz, 1H), 2.41 (s, 3H), 1.73 (d, J=7.0 Hz, 3H), 1.41 (d, J=6.9 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 188.4, 169.7, 143.6, 139.2, 136.6, 133.0, 131.0, 129.7, 128.0, 127.9, 127.1, 126.0, 124.6, 122.6, 121.8, 119.4, 115.9, 112.8, 111.6, 46.9, 39.8, 35.6, 21.8, 21.6, 21.0. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{29}H_{29}N_2O_3S_3$: 549.1340; found: 549.1345.

***N*-(3-(1-(1,3-Dithiolan-2-ylidene)-2-oxo-2-phenyl-ethyl)-1-allyl-1H-indol-2-yl)-4-methyl-benzene-sulfonamide (5d)**: 112 mg, 68% yield, yellow solid, m.p.: 200–201 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J=8.2 Hz, 2H), 7.28 (d, J=8.0 Hz, 1H), 7.22–7.11 (m, 3H), 7.11–7.05 (m, 4H), 7.03–6.93 (m, 3H), 5.66 (ddt, J=15.0, 9.7, 4.7 Hz, 1H), 5.47 (s, 1H), 4.90–4.75 (m, 2H), 4.72–4.59 (m, 1H), 4.43 (d, J=17.1 Hz, 1H), 3.25 (dt, J=9.3, 4.8 Hz, 2H), 3.09 (dt, J=10.0, 4.9 Hz, 1H), 2.88 (ddd, J=11.2, 9.3, 6.9 Hz, 1H), 2.26 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 188.6, 169.4, 143.6, 139.4, 136.5, 134.5, 133.0, 130.7, 129.6, 127.8, 127.8, 127.0, 126.2, 123.9, 123.2, 121.4, 120.0, 116.0, 115.6, 112.5, 110.7, 44.9, 39.6, 35.6, 21.7. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{29}H_{27}N_2O_3S_3$: 547.1184; found: 547.1148.

***N*-(3-(1-(1,3-Dithiolan-2-ylidene)-2-(2-methoxy-phenyl)-2-oxoethyl)-1-methyl-1H-indol-2-yl)-4-methyl-benzenesulfonamide (5e)**: 105 mg, 64% yield, green solid, m.p.: 235–236 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J=8.2 Hz, 2H), 7.38 (d, J=7.9 Hz, 1H), 7.26–7.15 (m, 5H), 7.14–7.05 (m, 1H), 6.91 (d, J=7.2 Hz, 1H), 6.80–6.67 (m, 2H), 6.54 (s, 1H), 3.65 (s, 3H), 3.51 (s, 3H), 3.35 (dd, J=8.4, 4.6 Hz, 2H), 3.17 (dt, J=11.2, 4.6 Hz, 1H), 2.85 (dt, J=11.3, 8.6 Hz, 1H), 2.42 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 189.7, 169.3, 155.6, 143.2, 137.0, 135.0, 131.0, 130.8, 129.7, 127.7, 127.5, 127.4, 124.2, 122.6, 121.3, 120.9, 119.6, 117.0, 111.3, 110.2, 55.6, 39.6, 35.7, 29.9, 21.9. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{28}H_{27}N_2O_4S_3$: 551.1133; found: 551.1126.

***N*-(3-(1-(1,3-Dithiolan-2-ylidene)-2-(2-fluorophenyl)-2-oxoethyl)-1-methyl-1H-indol-2-yl)-4-methylbenzene-sulfonamide (5f)**: 104 mg, 64% yield, yellow solid, m.p.: 244–245 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J=7.7 Hz, 2H), 7.42–7.17 (m, 6H), 7.10 (d, J=7.0 Hz, 1H), 6.97 (d, J=6.2 Hz, 1H), 6.89 (t, J=7.6 Hz, 2H), 5.97 (s, 1H), 3.69 (s, 3H), 3.38 (d, J=5.1 Hz, 2H), 3.28–3.17 (m, 1H), 3.08–2.91 (m, 1H), 2.41 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 186.5, 170.1, 159.5 (d, J_{C-F}=251.8 Hz), 143.7, 137.1, 135.1, 132.0 (d, J_{C-F}=8.4 Hz), 129.8, 129.0 (d, J_{C-F}=2.9 Hz), 128.7 (d, J_{C-F}=14.7 Hz), 127.4, 126.9, 124.2, 123.0, 123.9 (d, J_{C-F}=3.5 Hz), 121.3, 119.9, 116.9, 116.4, 116.2, 110.7, 110.2, 39.9, 35.9, 29.8, 21.9. $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ −112.9. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{27}H_{24}FN_2O_3S_3$: 539.0933; found: 539.0936.

***N*-(3-(1-(1,3-Dithiolan-2-ylidene)-2-(3-methoxy-phenyl)-2-oxoethyl)-1-methyl-1H-indol-2-yl)-4-methyl-benzenesulfonamide (5g)**: 114 mg, 69% yield, yellow solid, m.p.: 208–209 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J=8.3 Hz, 2H), 7.33 (dd, J=8.1, 3.7 Hz, 2H), 7.26 (t, J=7.7 Hz, 1H), 7.17 (d, J=8.1 Hz, 2H), 7.12–7.01 (m, 2H), 6.88 (d, J=7.6 Hz, 1H), 6.81 (dd, J=7.9, 2.2 Hz, 1H), 6.61 (d, J=1.6 Hz, 1H), 5.81 (s, 1H), 3.73 (s, 3H), 3.44–3.36 (m, 2H), 3.30–3.19 (m, 4H), 3.03 (ddd, J=11.3, 8.7, 7.1 Hz, 1H), 2.37 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 188.2, 169.2, 158.8, 143.7, 140.2, 136.7, 135.2, 129.8, 129.2, 127.2, 126.9, 124.0, 123.3, 121.4, 120.7, 120.2, 118.6, 115.9, 112.0, 111.9, 110.3, 54.9, 39.8, 35.6, 29.8, 21.8. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{28}H_{27}N_2O_4S_3$: 551.1133; found: 551.1122.

***N*-(3-(1-(1,3-Dithiolan-2-ylidene)-2-oxo-2-(p–tolyl)ethyl)-1-methyl-1H-indol-2-yl)-4-methyl-benzene-sulfonamide (5h)**: 108 mg, 67% yield, green solid, m.p.: 176–177 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J=7.9 Hz, 2H), 7.35 (d, J=8.3 Hz, 2H), 7.30–7.24 (m, 1H), 7.22–7.05 (m, 5H), 6.90 (d, J=7.7 Hz, 2H), 5.86 (s, 1H), 3.74 (s, 3H), 3.44–3.28 (m, 2H), 3.21 (dd, J=10.9, 4.9 Hz, 1H), 2.98 (dd, J=18.8, 7.9 Hz, 1H), 2.36 (s, 3H), 2.25 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 188.5, 168.1, 143.6, 141.7, 136.7, 136.2, 135.2, 129.7, 128.7, 128.3, 127.1, 126.7, 123.8, 123.1, 121.5, 119.9, 116.0, 111.6, 110.3, 39.7, 35.6, 29.8, 21.8, 21.5. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{28}H_{27}N_2O_3S_3$: 535.1184; found: 535.1179.

***N*-(3-(1-(1,3-Dithiolan-2-ylidene)-2-oxo-2-(4-(trifluoromethyl)phenyl)ethyl)-1-methyl-1H-indol-2-yl)-4-methylbenzenesulfonamide (5i)**: 115 mg, 65% yield, yellow solid, m.p.: 205–206 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J=8.1 Hz, 2H), 7.35–7.27 (m, 5H), 7.25 (d, J=9.9 Hz, 1H), 7.19 (d, J=7.9 Hz, 1H), 7.14 (d, J=8.2 Hz, 2H), 7.03 (t, J=7.5 Hz, 1H), 6.01 (s, 1H), 3.75 (s, 3H), 3.51–3.41 (m, 2H), 3.27 (dt, J=11.3, 5.8 Hz, 1H), 3.14 (dt, J=11.4, 7.4 Hz, 1H), 2.32 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 187.1, 170.6, 144.0, 142.1, 136.8, 135.2, 132.28 (q, J_{C-F}=65.1, 32.5 Hz), 129.8, 128.7, 127.1, 126.8, 124.73 (q, J_{C-F}=3.5 Hz), 123.9, 123.5, 121.0, 120.4, 115.7, 111.5, 110.4, 40.1, 35.6, 30.0, 21.8. $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ −63.0. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{28}H_{24}F_3N_2O_3S_3$: 589.0901; found: 589.0880.

***N*-(3-(1-(1,3-Dithiolan-2-ylidene)-2-(4-methoxy-phenyl)-2-oxoethyl)-1-methyl-1H-indol-2-yl)-4-methyl-benzenesulfonamide (5j)**: 117 mg, 71% yield, yellow solid, m.p.: 180–181 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J=7.9 Hz, 2H), 7.35 (t, J=8.3 Hz, 2H), 7.31–7.22 (m, 3H), 7.15 (d, J=7.9 Hz, 2H), 7.09 (t, J=7.4 Hz, 1H), 6.60 (d, J=8.6 Hz, 2H), 6.20 (s, 1H), 3.78 (s, 3H), 3.73 (s, 3H), 3.34 (t, J=6.2 Hz, 2H), 3.25–3.13 (m, 1H), 3.06–2.92 (m, 1H), 2.35 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 187.7, 167.0, 161.9, 143.6, 136.6, 135.1, 131.1, 130.7, 129.6, 127.0, 126.8, 123.7, 123.0,

121.4, 119.9, 116.0, 113.1, 111.6, 110.2, 55.3, 39.6, 35.5, 29.9, 21.7. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{28}H_{27}N_2O_4S_3$: 551.1133; found: 551.1122.

***N*-(3-(2-(4-Chlorophenyl)-1-(1,3-dithiolan-2-ylidene)-2-oxoethyl)-1-methyl-1H-indol-2-yl)-4-methylbenzene-sulfonamide (5k)**: 107 mg, 65% yield, yellow solid, m.p.: 212–213 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J=8.2 Hz, 2H), 7.34 (d, J=8.3 Hz, 1H), 7.26 (t, J=7.7 Hz, 1H), 7.22 (d, J=8.0 Hz, 1H), 7.17–7.10 (m, 4H), 7.08–7.00 (m, 3H), 5.96 (s, 1H), 3.77 (s, 3H), 3.46–3.37 (m, 2H), 3.25 (dt, J=11.1, 5.5 Hz, 1H), 3.10 (dt, J=11.4, 7.4 Hz, 1H), 2.33 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 187.1, 169.4, 143.9, 137.4, 137.2, 136.7, 135.2, 129.9, 129.8, 128.1, 127.1, 126.7, 123.8, 123.4, 121.2, 120.3, 115.8, 111.6, 110.4, 40.0, 35.6, 30.0, 21.8. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{27}H_{24}ClN_2O_3S_3$: 555.0638; found: 555.0648.

***N*-(3-(1-(1,3-Dithiolan-2-ylidene)-2-oxo-2-(thiophen-2-yl)-ethyl)-1-methyl-1H-indol-2-yl)-4-methylbenzene-sulfonamide (5l)**: 99 mg, 63% yield, yellow solid, m.p.: 198–199 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J=8.2 Hz, 2H), 7.37 (d, J=8.3 Hz, 1H), 7.29–7.21 (m, 2H), 7.16 (d, J=7.9 Hz, 1H), 7.00 (t, J=7.5 Hz, 1H), 6.92 (d, J=8.1 Hz, 2H), 6.83 (s, 1H), 6.64–6.58 (m, 1H), 6.51 (d, J=3.7 Hz, 1H), 3.92 (s, 3H), 3.53–3.35 (m, 2H), 3.16 (t, J=6.5 Hz, 2H), 2.27 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 178.8, 168.8, 143.7, 143.2, 136.1, 135.1, 132.9, 132.7, 129.2, 127.5, 127.2, 126.8, 124.8, 123.3, 120.9, 120.5, 115.0, 110.9, 110.1, 40.0, 34.9, 30.1, 21.7. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{25}H_{23}N_2O_3S_4$: 527.0592; found: 527.0591.

***N*-(3-(1,1-Bis(methylthio)-3-oxo-3-phenylprop-1-en-2-yl)-1-methyl-1H-indol-2-yl)-4-methylbenzene-sulfonamide (5m)**: 74 mg, 47% yield, yellow solid, m.p.: 186–187 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, 1H), 7.97–7.87 (m, 2H), 7.79 (d, J=8.3 Hz, 2H), 7.50 (ddd, J=6.5, 2.5, 1.2 Hz, 1H), 7.46–7.38 (m, 3H), 7.34 (d, J=8.2 Hz, 1H), 7.29–7.20 (m, 3H), 7.19–7.12 (m, 1H), 3.86 (s, 3H), 2.39 (s, 3H), 2.09 (s, 3H), 1.93 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 196.6, 143.6, 139.2, 137.7, 136.8, 135.4, 134.6, 133.1, 130.1, 129.7, 129.2, 128.6, 127.8, 124.4, 122.6, 120.4, 120.1, 110.5, 104.5, 30.8, 21.8, 17.8, 16.3. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{27}H_{27}N_2O_3S_3$: 523.1184; found: 523.1171.

***N*-(3-(1-(1,3-Dithiolan-2-ylidene)-2-oxo-2-phenyl-ethyl)-1,4-dimethyl-1H-indol-2-yl)-4-methylbenzene-sulfonamide (5n)**: 88 mg, 55% yield, yellow solid, m.p.: 156–157 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J=8.2 Hz, 2H), 7.21–7.13 (m, 3H), 7.13–7.05 (m, 2H), 7.04–6.94 (m, 4H), 6.74 (d, J=5.8 Hz, 1H), 5.95 (s, 1H), 3.68 (s, 3H), 3.39–3.24 (m, 2H), 3.09 (dt, J=12.1, 6.2 Hz, 1H), 3.04–2.91 (m, 1H), 2.22 (s, 3H), 2.19 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 187.0, 170.6, 143.7, 138.7, 137.0, 135.6, 131.5, 130.9, 129.7, 128.7, 127.8, 126.9, 126.6, 123.5, 123.3, 122.1, 117.5, 112.1, 107.9, 40.2, 35.0, 30.2, 21.7, 19.0. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{28}H_{27}N_2O_3S_3$: 535.1184; found: 535.1159.

***N*-(3-(1-(1,3-Dithiolan-2-ylidene)-2-oxo-2-phenyl-ethyl)-5-fluoro-1-methyl-1H-indol-2-yl)-4-methyl-benzenesulfonamide (5o)**: 113 mg, 70% yield, brown solid, m.p.: 190–191 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J=7.8 Hz, 2H), 7.32–7.24 (m, 2H), 7.23–7.15 (m, 4H), 7.11 (t, J=7.4 Hz, 2H), 7.07–6.94 (m, 2H), 5.96 (s, 1H), 3.71 (s, 3H), 3.46–3.31 (m, 2H), 3.31–3.18 (m, 1H), 3.03 (dd, J=18.6, 7.9 Hz, 1H), 2.37 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 188.7, 169.1, 157.8 (d, J_{C-F}=236.1 Hz), 143.8, 138.9, 136.6, 131.6, 131.2, 129.7, 128.1, 128.0, 127.9, 127.0, 124.1, 124.0, 111.6 (d, J_{C-F}=4.8 Hz), 115.4, 111.8, 111.6, 111.2 (d, J_{C-F}=9.4 Hz), 106.1 (d, J_{C-F}=24.0 Hz), 39.8, 35.6, 30.0, 21.7. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ −122.8. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{27}H_{24}FN_2O_3S_3$: 539.0933; found: 539.0964.

***N*-(3-(1-(1,3-Dithiolan-2-ylidene)-2-oxo-2-phenyl-ethyl)-6-methoxy-1-methyl-1H-indol-2-yl)-4-methyl-benzenesulfonamide (5p)**: 104 mg, 63% yield, yellow solid, m.p.: 213–214 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J=8.1 Hz, 2H), 7.28–7.17 (m, 2H), 7.15–7.08 (m, 4H), 7.03 (t, J=7.6 Hz, 2H), 6.68 (d, J=9.3 Hz, 2H), 5.52 (s, 1H), 3.81 (s, 3H), 3.61 (s, 3H), 3.32 (dd, J=9.1, 5.1 Hz, 2H), 3.23–3.11 (m, 1H), 2.96 (dd, J=17.1, 9.8 Hz, 1H), 2.29 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 188.5, 168.8, 157.3, 143.7, 139.1, 136.7, 136.0, 131.2, 129.8, 128.2, 128.0, 127.2, 125.3, 122.4, 118.0, 116.1, 111.9, 110.3, 93.3, 55.7, 39.8, 35.6, 29.8, 21.8. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{28}H_{27}N_2O_4S_3$: 551.1133; found: 551.1123.

***N*-(3-(1-(1,3-Dithiolan-2-ylidene)-2-oxo-2-phenyl-ethyl)-6-fluoro-1-methyl-1H-indol-2-yl)-4-methyl-benzenesulfonamide (5q)**: 113 mg, 70% yield, green solid, m.p.: 210–211 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J=8.2 Hz, 2H), 7.29 (t, J=7.2 Hz, 1H), 7.22 (dd, J=8.7, 5.3 Hz, 1H), 7.19–7.13 (m, 4H), 7.10 (t, J=7.6 Hz, 2H), 7.00 (dd, J=9.6, 2.0 Hz, 1H), 6.83 (dt, J=9.4, 2.2 Hz, 1H), 5.73 (s, 1H), 3.68 (s, 3H), 3.46–3.34 (m, 2H), 3.26 (dt, J=10.6, 5.2 Hz, 1H), 3.05 (dt, J=11.3, 7.8 Hz, 1H), 2.35 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 188.5, 169.1, 160.5 (d, J_{C-F}=240.0 Hz), 143.8, 138.9, 136.6, 135.3 (d, J_{C-F}=12.1 Hz), 131.2, 129.8, 128.1, 128.0, 127.1, 126.9, 126.9, 122.6 (d, J_{C-F}=9.8 Hz), 120.2, 115.6, 112.0, 109.0 (d, J_{C-F}=24.6 Hz), 96.7 (d, J_{C-F}=26.3 Hz), 39.9, 35.7, 30.0, 21.8. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ −118.1. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{27}H_{24}FN_2O_3S_3$: 539.0933; found: 539.0908.

***N*-(3-(1-(1,3-Dithiolan-2-ylidene)-2-oxo-2-phenyl-ethyl)-6-chloro-1-methyl-1H-indol-2-yl)-4-methyl-benzenesulfonamide (5r)**: 109 mg, 66% yield, brown solid, m.p.: 207–208 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J=8.2 Hz, 2H), 7.34 (d, J=1.1 Hz, 1H), 7.30 (t, J=7.1 Hz, 1H), 7.26 (s, 1H), 7.23 (d, J=8.5 Hz, 1H), 7.20–7.08 (m, 6H), 7.05 (dd, J=8.5, 1.4 Hz, 1H), 5.70 (s, 1H), 3.69 (s, 3H), 3.40 (t, J=6.2 Hz, 2H), 3.26 (dt, J=10.5, 5.1 Hz, 1H), 3.05 (dt, J=11.3, 8.0 Hz, 1H), 2.36 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 188.6, 169.3, 143.9, 138.9, 136.6, 135.6, 131.3, 129.8, 129.3, 128.1, 128.1, 127.4, 127.2, 122.5, 122.3, 120.9, 115.5, 112.0, 110.4, 39.9, 35.7, 30.0, 21.9. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{27}H_{24}ClN_2O_3S_3$: 555.0638; found: 555.0635.

***N*-(3-(1-(1,3-Dithiolan-2-ylidene)-2-oxo-2-phenyl-ethyl)-1,7-dimethyl-1H-indol-2-yl)-4-methylbenzene-sulfonamide (5s)**: 112 mg, 70% yield, yellow solid, m.p.: 177–178 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J=8.2 Hz, 2H), 7.18 (t, J=7.4 Hz, 1H), 7.11 (d, J=7.4 Hz, 2H), 7.09–6.97 (m, 5H), 6.91–6.80 (m, 2H), 5.72 (s, 1H), 3.85 (s, 3H), 3.34–3.19 (m, 2H), 3.09 (dt, J=10.5, 5.1 Hz, 1H), 2.89 (dt, J=11.2, 7.9 Hz, 1H), 2.67 (s, 3H), 2.25 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz,

$CDCl_3$) δ 188.5, 169.1, 143.6, 139.0, 136.7, 134.2, 131.0, 129.6, 128.1, 127.9, 127.0, 126.9, 126.0, 124.5, 121.8, 119.8, 119.3, 115.9, 111.7, 39.7, 35.5, 32.8, 21.7, 20.2. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{28}H_{27}N_2O_3S_3$: 535.1184; found: 535.1188.

***N*-(3-(1-(1,3-Dithiolan-2-ylidene)-2-(4-methoxy-phenyl)-2-oxoethyl)-5-fluoro-1-methyl-1H-indol-2-yl)-4-methylbenzenesulfonamide (5t)**: 114 mg, 67% yield, green solid, m.p.: 203–204 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J=8.1 Hz, 2H), 7.27 (d, J=6.4 Hz, 1H), 7.21 (d, J=8.7 Hz, 2H), 7.14 (d, J=8.0 Hz, 2H), 7.06–6.93 (m, 2H), 6.60 (d, J=8.7 Hz, 2H), 6.23 (s, 1H), 3.75 (s, 3H), 3.73 (s, 3H), 3.43–3.28 (m, 2H), 3.28–3.13 (m, 1H), 3.01 (dt, J=11.1, 7.5 Hz, 1H), 2.33 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 187.9, 167.0, 162.1, 157.9 (d, J_{C-F}=235.9 Hz), 143.7, 136.5, 131.7, 131.0, 130.7, 129.7, 129.2, 128.3, 127.1, 124.0 (d, J_{C-F}=9.8 Hz), 115.6, 113.2, 111.7 (d, J_{C-F}=26.3 Hz), 111.6 (d, J_{C-F}=4.8 Hz), 111.2 (d, J_{C-F}=9.5 Hz), 106.2 (d, J_{C-F}=24.0 Hz), 55.3, 39.7, 35.6, 30.2, 21.8. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ −122.9. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{28}H_{26}FN_2O_4S_3$: 569.1039; found: 569.1031.

***N*-(3-(1-(1,3-Dithiolan-2-ylidene)-2-oxo-2-(4-(trifluoromethyl)phenyl)ethyl)-1,7-dimethyl-1H-indol-2-yl)-4-methylbenzenesulfonamide (5u)**: 114 mg, 63% yield, green solid, m.p.: 225–226 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J=8.3 Hz, 2H), 7.37–7.27 (m, 4H), 7.13 (d, J=8.1 Hz, 2H), 7.01 (d, J=7.8 Hz, 1H), 6.95 (d, J=6.9 Hz, 1H), 6.92–6.85 (m, 1H), 5.93 (s, 1H), 3.99 (s, 3H), 3.53–3.40 (m, 2H), 3.26 (dt, J=11.3, 5.6 Hz, 1H), 3.12 (dt, J=11.4, 7.4 Hz, 1H), 2.78 (s, 3H), 2.32 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 187.0, 170.8, 144.0, 142.1, 136.8, 134.4, 132.3 (q, J_{C-F}=62.6, 32.3 Hz), 129.8, 128.7, 127.1, 126.9, 126.4, 124.8 (q, J_{C-F}=7.4, 3.7 Hz), 124.6, 122.1, 120.3, 119.0, 115.8, 111.7, 77.5, 77.2, 76.8, 40.0, 35.6, 33.0, 21.8, 20.4. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ −63.0. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{29}H_{26}F_3N_2O_3S_3$: 603.1058; found: 603.1022.

Indolin-2-one 6a; Typical Procedure for the Synthesis of Compounds 6

A mixture of 3-vinyl oxindole **3p** (74 mg, 0.2 mmol), MeI (43 mg, 0.3 mmol), K_2CO_3 (55 mg, 0.4 mmol), and DMF (2 mL) was stirred at ambient temperature for 12 h, and then evaporated all the volatiles under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: petroleum ether (60–90 °C)/AcOEt=10:1, v/v), affording **6a** as a yellow oil (69 mg, 90%).

3-(1,1-Bis(methylthio)-3-oxo-3-phenylprop-1-en-2-yl)-1,3-dimethylindolin-2-one (6a): 69 mg, 90% yield, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, J=7.2 Hz, 2H), 7.57–7.37 (m, 4H), 7.25–7.16 (m, 1H), 7.01 (td, J=7.6, 0.8 Hz, 1H), 6.78 (d, J=7.7 Hz, 1H), 3.21 (s, 3H), 1.88 (s, 3H), 1.72 (s, 3H), 1.23 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 195.4, 180.0, 148.7, 143.4, 137.6, 136.9, 135.5, 133.5, 129.7, 128.8, 128.0, 123.4, 123.0, 108.1, 52.3, 26.8, 24.3, 17.2, 15.8. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{21}H_{22}NO_2S_2$: 384.1092; found: 384.1088.

3-(1-(1,3-Dithiolan-2-ylidene)-2-oxo-2-phenylethyl)-1-methyl-3-(prop-2-yn-1-yl)indolin-2-one (6b): 112 mg, 92% yield, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, J=7.4 Hz, 2H), 7.57 (dd, J=15.5, 7.5 Hz, 2H), 7.48 (t, J=7.6 Hz, 2H), 7.33 (t, J=7.6 Hz, 1H), 7.13 (t, J=7.5 Hz, 1H), 6.83 (d, J=7.7 Hz, 1H), 3.29 (s, 3H), 3.24–3.10 (m, 3H), 3.01 (ddd, J=12.1, 9.7, 4.0 Hz, 2H), 2.81 (dd, J=16.0, 2.5 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 196.0, 176.6, 145.7, 144.5, 137.3, 133.6, 130.6, 130.2, 128.8, 128.8, 124.8, 124.2, 123.3, 107.7, 78.6, 70.9, 55.8, 38.8, 38.5, 27.4, 26.4. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{23}H_{20}NO_2S_2$: 406.0935; found: 406.0949.

3-(1-(1,3-Dithiolan-2-ylidene)-2-oxo-2-phenylethyl)-1-methyl-3-phenethylindolin-2-one (6c): 124 mg, 88% yield, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55–7.44 (m, 3H), 7.42–7.28 (m, 5H), 7.26–7.20 (m, 4H), 7.17 (t, J=7.6 Hz, 2H), 4.34 (t, J=6.7 Hz, 2H), 3.64 (t, J=6.4 Hz, 2H), 3.40 (s, 3H), 3.36 (t, J=6.3 Hz, 2H), 3.02 (t, J=6.7 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 191.0, 169.9, 148.2, 139.7, 137.8, 131.9, 130.5, 129.0, 128.5, 128.3, 127.5, 126.5, 125.8, 120.4, 119.9, 118.8, 116.6, 108.7, 94.8, 73.0, 40.1, 36.2, 35.5, 27.8. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{28}H_{26}NO_2S_2$: 472.1405; found: 472.1400.

3-Methyleneoxindole 7

A mixture of 3-vinyl oxindole **3p** (111 mg, 0.3 mmol), Et_3N (0.2 mL), and toluene (3 mL) was stirred at 80 °C for 24 h, cooled to ambient temperature, and then evaporated all the volatiles under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: petroleum ether (60–90 °C)/AcOEt=10:1, v/v), affording **7** as a yellow solid (83 mg, 75%).

3-(1,1-Bis(methylthio)-3-oxo-3-phenylpropan-2-ylidene)-1-methylindolin-2-one (7): 83 mg, 75% yield, yellow solid, m.p.: 132–133 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J=7.3 Hz, 2H), 7.61 (t, J=7.4 Hz, 1H), 7.47 (t, J=7.7 Hz, 2H), 7.20 (t, J=7.7 Hz, 1H), 6.85 (d, J=8.7 Hz, 2H), 6.78 (d, J=7.8 Hz, 1H), 6.72 (t, J=7.6 Hz, 1H), 3.28 (s, 3H), 2.24 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 195.0, 167.0, 148.5, 143.1, 135.9, 134.6, 130.3, 129.8, 129.0, 124.3, 122.5, 120.1, 108.3, 47.8, 26.1, 16.3. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{20}H_{20}NO_2S_2$: 370.0935; found: 370.0919.

Bi(heteroaryl) Compound 8

A mixture of 3-vinyl indole **5m** (157 mg, 0.3 mmol), hydrazine hydrate (150 mg, 3 mmol), and EtOH (3 mL) was stirred at 80 °C for 24 h and then evaporated all the volatiles under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: petroleum ether (60–90 °C)/AcOEt=10:1, v/v), affording **8** as a yellow oil (128 mg, 88%).

4-Methyl-N-(1-methyl-3-(5-(methylthio)-3-phenyl-1H-pyrazol-4-yl)-1H-indol-2-yl)benzene-sulfonamide (8): 128 mg, 88% yield, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.35–7.25 (m, 3H), 7.18 (s, 1H), 7.17–7.05 (m, 4H), 6.97 (d, J=7.5 Hz, 2H), 6.79–6.70 (m, 2H), 6.66 (d, J=8.1 Hz, 2H), 3.88 (s, 3H), 2.30 (s, 3H), 1.88 (s, 3H). ^{13}C{^{1}H} NMR

(100 MHz, $CDCl_3$) δ 143.9, 143.5, 142.2, 136.0, 135.7, 129.3, 128.6, 128.6, 127.4, 126.7, 126.2, 124.1, 122.9, 121.0, 119.9, 110.5, 110.0, 102.1, 30.1, 21.3, 16.0. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{26}H_{25}N_4O_2S_2$: 489.1419; found: 489.1411.

Acknowledgements

We are grateful to the National Natural Science Foundation of China (22171261 and 21871253) for support of this research.

References

[1] a) S. K. Sinha, S. Guin, S. Maiti, J. P. Biswas, S. Porey, D. Maiti, *Chem. Rev.* **2022**, *122*, 5682–5841; b) N. Holmberg-Douglas, D. A. Nicewicz, *Chem. Rev.* **2022**, *122*, 1925–2016; c) Y. Kim, C.-J. Li, *Green Synth. Catal.* **2020**, *1*, 1–11; d) B. Xu, M.-L. Li, X.-D. Zuo, S.-F. Zhu, Q.-L. Zhou, *J. Am. Chem. Soc.* **2015**, *137*, 8700–8703; e) B. Ma, Z. W. Chu, B. Huang, Z. L. Liu, L. Liu, J. L. Zhang, *Angew. Chem. Int. Ed.* **2017**, *56*, 2749–2753; *Angew. Chem.* **2017**, *129*, 2793–2797.

[2] a) Y. He, Z. L. Huang, K. K. Wu, J. Ma, Y.-G. Zhou, Z. K. Yu, *Chem. Soc. Rev.* **2022**, *51*, 2759–2852; b) X.-S. Liu, Z. Q. Tang, Z.-Y. Si, Z. K. Zhang, L. Zhao, L. Liu, *Angew. Chem. Int. Ed.* **2022**, *61*, e202208874; c) Z. Y. Li, Y. Chen, C. Wang, G. Y. Xu, Y. Shao, X. H. Zhang, S. B. Tang, J. T. Sun, *Angew. Chem. Int. Ed.* **2021**, *60*, 25714–25718; d) D.-X. Zhu, H. Xia, J.-G. Liu, L. W. Chung, M.-H. Xu, *J. Am. Chem. Soc.* **2021**, *143*, 2608–2619; e) B. D. Bergstrom, L. A. Nickerson, J. T. Shaw, L. W. Souza, *Angew. Chem. Int. Ed.* **2021**, *60*, 6864–6878; f) S. Kumar, S. Nunewar, S. Oluguttula, S. Nanduri, V. Kanchupalli, *Org. Biomol. Chem.* **2021**, *19*, 1438–1458; g) R. Hommelsheim, Y. J. Guo, Z. Yang, C. Empel, R. M. Koenigs, *Angew. Chem. Int. Ed.* **2019**, *58*, 1203–1207; *Angew. Chem.* **2019**, *131*, 1216–1220; h) G. L. Xiao, T. T. Chen, C. Q. Ma, D. Xing, W. H. Hu, *Org. Lett.* **2018**, *20*, 4531–4535; i) M. P. Doyle, R. Duffy, M. Ratnikov, L. Zhou, *Chem. Rev.* **2010**, *110*, 704–724.

[3] a) J. D. Pizarro, I. L. Schmidtke, A. Nova, M. R. Fructos, P. J. Pérez, *ACS Catal.* **2022**, *12*, 6851–6856; b) G. Y. Xu, M. R. Huang, T. Zhang, Y. Shao, S. B. Tang, H. Cao, X. H. Zhang, J. T. Sun, *Org. Lett.* **2022**, *24*, 2809–2814; c) L. H. Kong, X. Han, H. H. Chen, H. M. Sun, Y. Lan, X. W. Li, *ACS Catal.* **2021**, *11*, 4929–4935; d) Z. Z. Yu, G. H. Li, J. L. Zhang, L. Liu, *Org. Chem. Front.* **2021**, *8*, 3770–3775; e) A. D. Yamaguchi, K. M. Chepiga, J. Yamaguchi, K. Itami, H. M. L. Davies, *J. Am. Chem. Soc.* **2015**, *137*, 644–647; f) Z. Z. Yu, B. Ma, M. J. Chen, H.-H. Wu, L. Liu, J. L. Zhang, *J. Am. Chem. Soc.* **2014**, *136*, 6904–6907; g) Y. M. Xi, Y. J. Su, Z. Y. Yu, B. L. Dong, E. J. McClain, Y. Lan, X. D. Shi, *Angew. Chem. Int. Ed.* **2014**, *53*, 9817–9821; *Angew. Chem.* **2014**, *126*, 9975–9979.

[4] a) P. N. Bagle, M. V. Mane, S. P. Sancheti, A. B. Gade, S. R. Shaikh, M.-H. Baik, N. T. Patil, *Org. Lett.* **2019**, *21*, 335–339; b) S. H. Yun, L. K. Xia, S. H. Kim, Y. R. Lee, *Asian J. Org. Chem.* **2016**, *5*, 1142–1147; c) Y. L. Zhao, Q. Z. Duan, Y. Y. Zhou, Q. Y. Yao, Y. Z. Li, *Org. Biomol. Chem.* **2016**, *14*, 2177–2181.

[5] a) L. Jin, X. Zhou, Y. B. Zhao, J. Guo, D. W. Stephan, *Org. Biomol. Chem.* **2022**, DOI: 10.1039/d2ob01048 h; b) C.-Y. Chen, J.-H. Zhao, L.-X. Xiong, F. Y. Wang, G. C. Yang, C. Ma, *Org. Biomol. Chem.* **2022**, *20*, 4101–4104; c) A. Dasgupta, E. Richards, R. L. Melen, *ACS Catal.* **2022**, *12*, 442–452; d) K. X. Dong, X.-S. Liu, X. Y. Wei, Y. T. Zhao, L. Liu, *Green Synth. Catal.* **2021**, *2*, 385–388; e) Q. Zhang, X.-F. Zhang, M. Li, C. Li, J.-Q. Liu, Y.-Y. Jiang, X. Ji, L. Liu, Y.-C. Wu, *J. Org. Chem.* **2019**, *84*, 14508–14519; f) S.-S. Meng, X. W. Tang, X. Luo, R. B. Wu, J.-L. Zhao, A. S. C. Chan, *ACS Catal.* **2019**, *9*, 8397–8403; g) S. E. Cleary, X. Li, L.-C. Yang, K. N. Houk, X. Hong, M. Brewer, *J. Am. Chem. Soc.* **2019**, *141*, 3558–3565; h) H. H. San, S.-J. Wang, M. Jiang, X.-Y. Tang, *Org. Lett.* **2018**, *20*, 4672–4676; i) Y. Qin, L. H. Zhu, S. Z. Luo, *Chem. Rev.* **2017**, *117*, 9433–9520.

[6] a) Z. Z. Yu, Y. F. Li, J. M. Shi, B. Ma, L. Liu, J. L. Zhang, *Angew. Chem. Int. Ed.* **2016**, *55*, 14807–14811; *Angew. Chem.* **2016**, *128*, 15027–15031; b) A. Dasgupta, R. Babaahmadi, B. Slater, B. F. Yates, A. Ariafard, R. L. Melen, *Chem.* **2020**, *6*, 2364–2381; c) F. F. He, R. M. Koenigs, *Org. Lett.* **2021**, *23*, 5831–5835.

[7] a) S. I. Lee, G.-S. Hwang, D. H. Ryu, *J. Am. Chem. Soc.* **2013**, *135*, 7126–7129; b) S. I. Lee, B. C. Kang, G.-S. Hwang, D. H. Ryu, *Org. Lett.* **2013**, *15*, 1428–1431; c) Z. K. Xue, Y. Li, S. Z. Luo, *ACS Catal.* **2020**, *10*, 10989–10998.

[8] a) J. G. Yang, S. M. Liu, J. Gui, D. K. Xiong, J. S. Li, Z. M. Wang, J. Ren, *J. Org. Chem.* **2022**, *87*, 6352–6361; b) V. Pozhydaiev, M. Power, V. Gandon, J. Moran, D. Leboeuf, *Chem. Commun.* **2020**, *56*, 11548–11564; c) J. L. Röckl, D. Pollok, R. Franke, S. R. Waldvogel, *Acc. Chem. Res.* **2020**, *53*, 45–61.

[9] a) R. H. Vekariya, J. Aubé, *Org. Lett.* **2016**, *18*, 3534–3537; b) H. F. Motiwala, C. Fehl, S.-W. Li, E. Hirt, P. Porubsky, J. Aubé, *J. Am. Chem. Soc.* **2013**, *135*, 9000–9009.

[10] a) Y. Tian, X. Xu, L. Zhang, J. Qu, *Org. Lett.* **2016**, *18*, 268–271; b) G.-X. Li, J. Qu, *Chem. Commun.* **2010**, *46*, 2653–2655.

[11] a) X. Ji, Z. K. Zhang, Y. Z. Wang, Y. Z. Han, H. L. Peng, F. Z. Lia, L. Liu, *Org. Chem. Front.* **2021**, *8*, 6916–6922; b) C. Empel, D. Verspeek, S. Jana, R. M. Koenigs, *Adv. Synth. Catal.* **2020**, *362*, 4716–4722; c) Y. X. Zhu, I. Colomer, A. L. Thompson, T. J. Donohoe, *J. Am. Chem. Soc.* **2019**, *141*, 6489–6493.

[12] a) B. Dahms, P. J. Kohlpaintner, A. Wiebe, R. Breinbauer, D. Schollmeyer, S. R. Waldvogel, *Chem. Eur. J.* **2019**, *25*, 2713–2716; b) P. A. Champagne, Y. Benhassine, J. Desroches, J.-F. Paquin, *Angew. Chem. Int. Ed.* **2014**, *53*, 13835–13839; *Angew. Chem.* **2014**, *126*, 14055–14059.

[13] a) S. D. Wang, G. Force, R. Guillot, J.-F. Carpentier, Y. Sarazin, C. Bour, V. Gandon, D. Leboeuf, *ACS Catal.* **2020**, *10*, 10794–10802; b) C. X. Qi, V. Gandon, D. Leboeuf, *Angew. Chem. Int. Ed.* **2018**, *57*, 14245–14249; *Angew. Chem.* **2018**, *130*, 14441–14445.
[14] I. Colomer, *ACS Catal.* **2020**, *10*, 6023–6029.
[15] a) S. D. Wang, G. Force, J.-F. Carpentier, Y. Sarazin, C. Bour, V. Gandon, D. Leboeuf, *Org. Lett.* **2021**, *23*, 2565–2570; b) A. Chatupheeraphat, M. Rueping, M. Magre, *Org. Lett.* **2019**, *21*, 9153–9157.
[16] a) R. Babaahmadi, A. Dasgupta, C. J. T. Hyland, B. F. Yates, R. L. Melen, A. Ariafard, *Chem. Eur. J.* **2022**, *28*, e202104376; b) A. Dasgupta, R. Babaahmadi, S. Pahar, K. Stefkova, L. Gierlichs, B. F. Yates, A. Ariafard, R. L. Melen, *Angew. Chem. Int. Ed.* **2021**, *60*, 24395–24399.
[17] a) P. Wu, Y. He, H. M. Wang, Y.-G. Zhou, Z. K. Yu, *Org. Lett.* **2020**, *22*, 310–315; b) J. Lou, Y. He, Y. L. Li, Z. K. Yu, *Adv. Synth. Catal.* **2019**, *361*, 3787–3799; c) Q. N. Wang, X. G. Yang, P. Wu, Z. K. Yu, *Org. Lett.* **2017**, *19*, 6248–6251; d) H. F. Yu, W. W. Jin, C. L. Sun, J. P. Chen, W. M. Du, S. B. He, Z. K. Yu, *Angew. Chem. Int. Ed.* **2010**, *49*, 5792–5797; *Angew. Chem.* **2010**, *122*, 5928–5933.
[18] C. Xu, M. Wang, Q. Liu, *Adv. Synth. Catal.* **2019**, *361*, 1208–1229.
[19] a) Z. L. Huang, Y. He, L. D. Wang, J. Y. Li, B.-H. Xu, Y.-G. Zhou, Z. K. Yu, *J. Org. Chem.* **2022**, *87* 4424–4437; b) G. R. Sheng, K. Huang, Z. H. Chi, H. L. Ding, Y. P. Xing, P. Lu, Y. G. Wang, *Org. Lett.* **2014**, *16*, 5096–5099.
[20] Y. Y. Khomutnyk, A. J. Argüelles, G. A. Winschel, Z. K. Sun, P. M. Zimmerman, P. Nagorny, *J. Am. Chem. Soc.* **2016**, *138*, 444–456.
[21] C. Tang, Q. M. Liang, A. R. Jupp, T. C. Johnstone, R. C. Neu, D. T. Song, S. Grimme, D. W. Stephan, *Angew. Chem. Int. Ed.* **2017**, *56*, 16588–16592; *Angew. Chem.* **2017**, *129*, 16815–16819.

