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# Synthesis of 1-Alkyl-3-(2-oxo-2-aryl/alkyl-ethyl)indolin-2-ones through Gold/Brønsted Acid Relay Actions: Observation of Selective C=C Bond Cleavage of Enaminones

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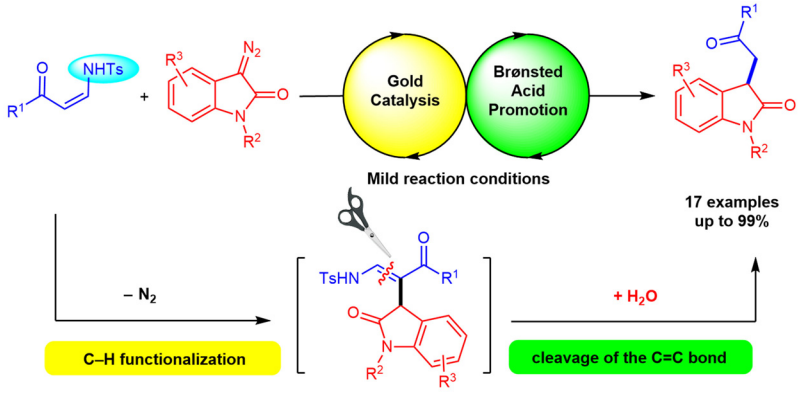


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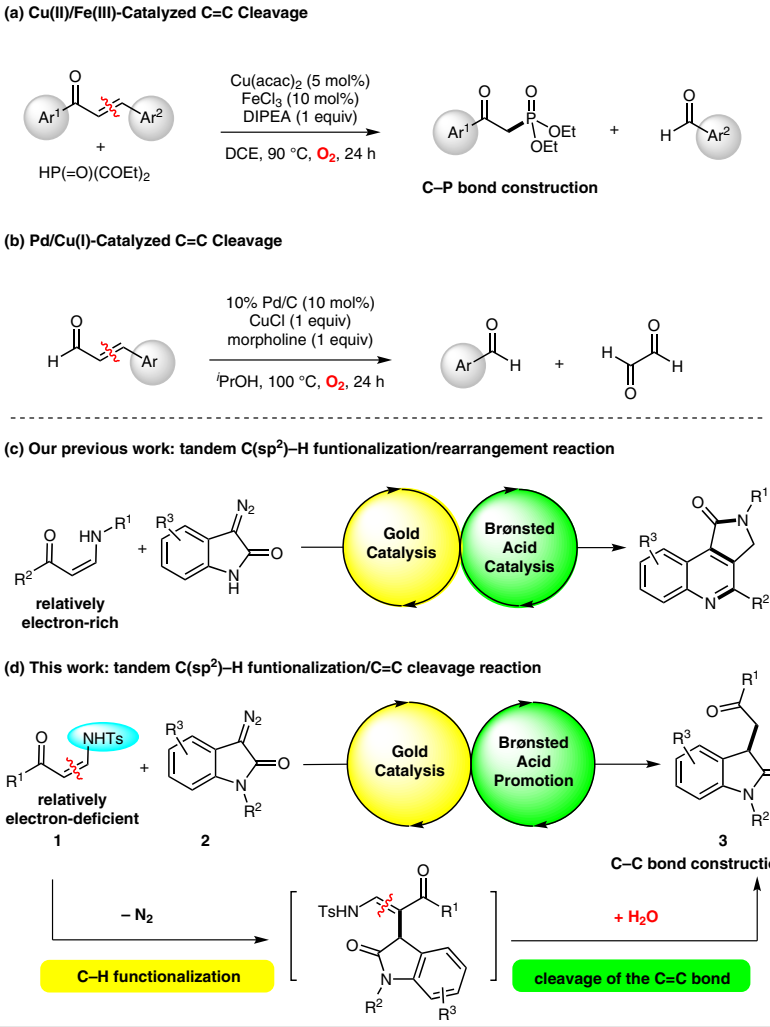
**Abstract** A novel gold(I)/Brønsted acid sequential catalyzed/promoted procedure to synthesize 1-alkyl-3-(2-oxo-2-aryl/alkyl-ethyl)indolin-2-ones under mild reaction conditions is developed. This methodology is realized by relay actions of gold and a Brønsted acid in a one-pot multistep manner. The gold(I)-catalyzed chemoselective C($sp^2$)-H functionalization of enaminones and Brønsted acid promoted cleavage of the C=C bond are integrated effectively. Based on the results of control experiments and ESI-MS analysis, a possible reaction mechanism is proposed.

**Key words** gold(I) catalysis, Brønsted acid promotion, C($sp^2$)–H functionalization, carbon–carbon bond activation, one-pot synthesis

The cleavage of carbon–carbon bonds is a basic challenge in chemistry.[1] Because of the weaker interactions with metal catalysts and the lower polarization, the cleavage of carbon–carbon bonds is relatively difficult. With an irreplaceable role in the petroleum industry, C–C bond cleavage has been a topic of special interest in organic chemistry and has attracted significant attention in recent years. After years of development, a number of excellent approaches for the cleavage of carbon–carbon bonds,[2] including the deformylation or deacetylation of 1,3-dicarbonyl compounds[2f–h] and the cleavage of carbon–carbon double bonds, have been described in the literature. The cleavage of carbon–carbon double bonds mainly occurs via oxidative cleavage reactions,[3] metathesis reactions,[4] and so on.[5] α,β-Unsaturated carbonyl compounds are very useful building blocks in organic synthesis. Decarbonylation or decarboxylation [cleavage of a C($sp^2$)–C(C=O) bond] have been widely reported,[6] but cleavage of the carbon–carbon double bond of α,β-unsaturated carbonyl compounds was rarely explored. In 2016, Song and co-workers realized an elegant Cu(II)/Fe(III)-catalyzed C=C cleavage of α,β-unsaturated carbonyl compounds with H-phosphonates leading to β-ketophosphonates (Scheme 1, a).[7] Sajiki and co-workers reported an excellent procedure for the Pd(0)/Cu(I)-catalyzed regioselective C=C bond cleavage of cinnamaldehydes for the preparation of aromatic aldehydes (Scheme 1, b).[8] In, 1987, Eicher and co-workers disclosed the C=C bond cleavage of an enaminone under acidic reflux conditions,[9] however, only one example was reported.

As a type of α,β-unsaturated carbonyl compound, enaminones are widely used in organic synthesis.[10] As part of our ongoing interest in the development of enaminone chemistry,[11] we previously disclosed Au-catalyzed tandem reactions involving chemo- and diastereoselective C($sp^2$)–H functionalization of relatively electron-rich enaminones for the synthesis of pyrrolo[3,4-*c*]-quinolin-1-one derivatives (Scheme 1, c).[11a] Interestingly, when the substituent on the nitrogen atom of the enaminones was changed to a tosyl group, selective C=C bond cleavage was realized to afford 1-alkyl-3-(2-oxo-2-aryl/alkyl-ethyl)indolin-2-ones (Scheme 1, d).

Herein, we report a gold(I)/Brønsted acid sequential catalyzed/promoted procedure to synthesize 1-alkyl-3-(2-oxo-2-aryl/alkyl-ethyl)indolin-2-ones. The challenges associated with this tandem reaction are as follows: (1) To realize selective C($sp^2$)–H functionalization of relatively electron-deficient enaminones over the N–H insertion reaction,[12] which is usually observed in analogous procedures. (2) Selective cleavage of the carbon–carbon double bond rather than decarbonylation or decarboxylation.




**Scheme 1** Examples of C=C bond cleavage of α,β-unsaturated carbonyl compounds

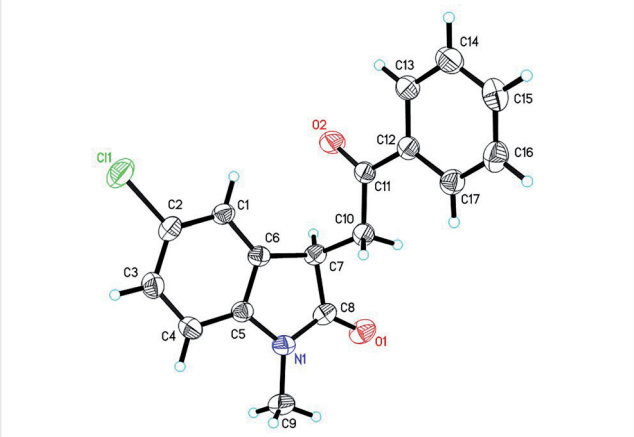
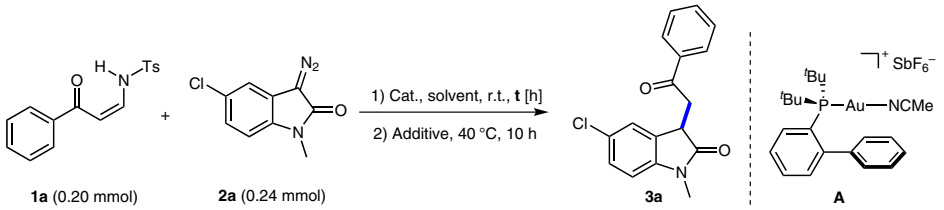



**Figure 1** X-ray crystal structure of **3a**

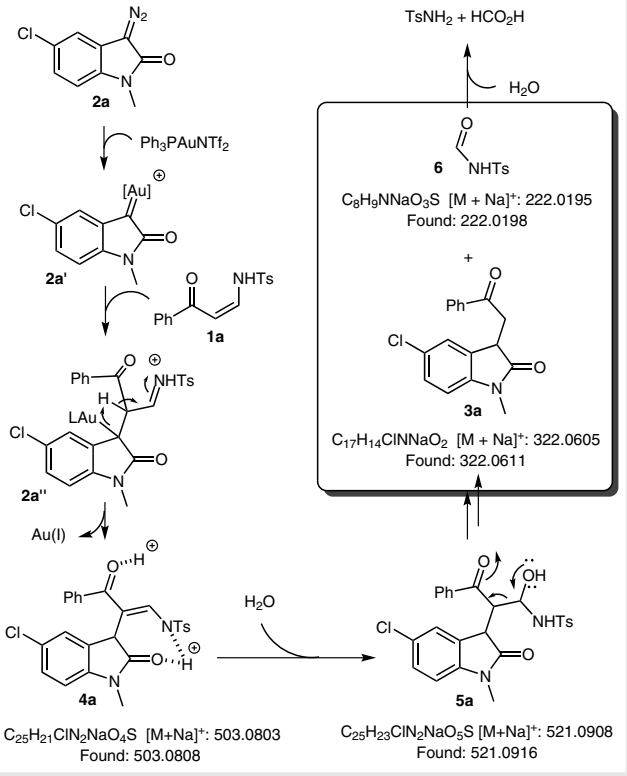
Initially, our investigation began with the attempted coupling of (*Z*)-4-methyl-*N*-(3-oxo-3-phenylprop-1-en-1-yl)benzenesulfonamide (**1a**) and 5-chloro-3-diazo-1-methylindolin-2-one (**2a**), which were readily prepared according to the literature methods.[13] Firstly, the reaction of **1a** with **2a** was carried out using $Ph_3PAuNTf_2$ (5 mol%) as the catalyst in air. However, severe decomposition of **2a** was observed (Table 1, entry 1). So, we decided to add **2a** in dichloromethane (1 mL) within two hours by using a syringe pump and a major product was detected by TLC. Nevertheless, preliminary NMR characterization of the product gave an unclean spectrum. Interestingly, when the solvents were removed under reduced pressure in the presence of chloroform, a cleaner NMR spectrum was obtained. Encouraged by this discovery, we decided to remove dichloromethane under reduced pressure one hour after the addition of **2a**. Next, chloroform (4 mL) was added to the residue and the reaction was stirred at room temperature. To our delight,

**Table 1** Optimization of the Reaction Conditions[a]




| Entry | Catalyst (mol%) | Time (h) | Solvent | Additive | Yield (%)[b] |
|---|---|---|---|---|---|
| 1 | $Ph_3PAuNTf_2$ (5) | –[c] | $CH_2Cl_2$ | – | trace |
| 2 | $Ph_3PAuNTf_2$ (5) | 2 | $CH_2Cl_2$ | $CHCl_3$ | 58[d] |
| 3 | $Ph_3PAuNTf_2$ (5) | 2 | $CH_2Cl_2$ | $CHCl_3$ | 93 |
| 4 | $Ph_3PAuNTf_2$ (5) | 2 | $CHCl_3$ | $CHCl_3$ | 53 |
| 5 | $Ph_3PAuNTf_2$ (5) | 2 | $CH_2Cl_2$ | $HCl_{concd}$ | 98 |
| 6 | **A** (5) | 2 | $CH_2Cl_2$ | $HCl_{concd}$ | 87 |
| **7** | **$Ph_3PAuNTf_2$ (2)** | **2** | **$CH_2Cl_2$** | **$HCl_{concd}$** | **95** |
| 8 | $Ph_3PAuNTf_2$ (2) | 1 | $CH_2Cl_2$ | $HCl_{concd}$ | 86 |
| 9 | $Ph_3PAuNTf_2$ (2) | 3 | $CH_2Cl_2$ | $HCl_{concd}$ | 96 |
| 10 | $Ph_3PAuNTf_2$ (2) | 2 | $CH_2Cl_2$ | $HCl_{concd}$ | 95[e] |

[a] Reaction conditions: **2a** in $CH_2Cl_2$ (1.0 mL) was added to a solution of **1a** and the catalyst using a syringe pump with addition over the time listed. After 1 h, $HCl_{concd}$ (12 M, 40 µL, 2.4 equiv) was added [or $CH_2Cl_2$ was replaced with $CHCl_3$ (4 mL)].
[b] Yield of isolated product.
[c] Substrate **2a** (solid) was added in one portion.
[d] After **2a** had been added, the mixture was stirred at r.t. for 20 h.
[e] Reaction under a nitrogen atmosphere.

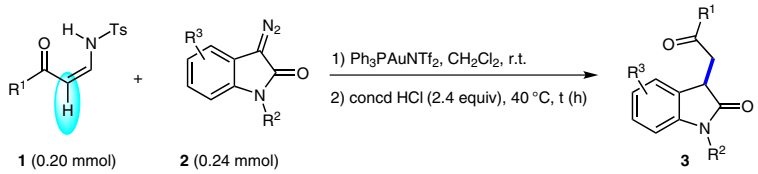



**Scheme 2** The possible reaction mechanism

pure product **3a**, which was fully confirmed by X-ray crystallography analysis (Figure 1),[14] was easily isolated in a yield of 58% (entry 2). Moreover, on raising the reaction temperature to 40 °C after the solvent was changed to chloroform, the yield of **3a** was increased to 93% (entry 3). When chloroform was used as the solvent instead of $CH_2Cl_2$, partial decomposition of the diazo compound was inevitable (entry 4). In order to avoid the decomposition of the diazo compound and simplify operations, dichloromethane was used as the solvent and $HCl_{concd}$ (40 µL, 2.4 equiv) was subsequently added (entry 5). As we expected, the tandem reaction took place smoothly and **3a** was obtained in an excellent yield (98%). Furthermore, JohnPhos(MeCN)$AuSbF_6$ (catalyst **A**) was also investigated (entry 6), but no better result was achieved. When the amount of $Ph_3PAuNTf_2$ was reduced to 2 mol%, the reaction proceeded successfully to afford a 95% yield of **3a** (entry 7). Reducing the time for the addition of **2a** led to partial decomposition and lowered the yield to 86% (entry 8). Increasing the time to three hours gave a similar result (entry 7 vs 9; 95% vs 96%). The use of a nitrogen atmosphere had no significant effect on the reaction outcome (entry 10).

With optimized reaction conditions in hand (Table 1, entry 7), we next examined the substrate scope (Table 2). A range of substituted diazoindolinones and enaminones were suitable for the reaction, offering the corresponding products **3a–q** in good to excellent yields. Firstly, the $R^3$

**Table 2** Reaction Scope[a]

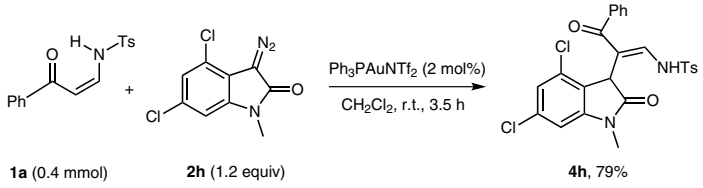



**1** (0.20 mmol) **2** (0.24 mmol) **3**

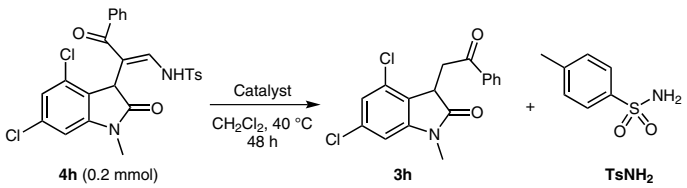
| Entry | $R^1$ | $R^2$ | $R^3$ | Time (h) | Product | Yield (%)[b] |
|---|---|---|---|---|---|---|
| 1 | Ph | Me | 5-Cl | 10 | **3a** | 95 |
| 2 | Ph | Me | 5-$O_2$N | 10 | **3b** | 71 |
| 3 | Ph | Me | 5-F | 10 | **3c** | 99 |
| 4 | Ph | Me | 5-Br | 10 | **3d** | 87 |
| 5 | Ph | Me | 5-H | 10 | **3e** | 82 |
| 6 | Ph | Me | 5-Me | 10 | **3f** | 86 |
| 7 | Ph | Me | 5-MeO | 10 | **3g** | 88 |
| 8 | Ph | Me | 4,6-$Cl_2$ | 79 | **3h** | 71 |
| 9 | Ph | 4-$O_2N(C_6H_4)CH_2$ | 5-Cl | 15 | **3i** | 78 |
| 10 | Ph | 4-Br($C_6H_4$)$CH_2$ | 5-Cl | 15 | **3j** | 85 |
| 11 | Ph | Bn | 5-Cl | 15 | **3k** | 85 |
| 12 | Ph | 4-Me($C_6H_4$)$CH_2$ | 5-Cl | 15 | **3l** | 74 |
| 13[c] | *t*-Bu | Me | 5-Cl | 48 | **3m** | 83 |
| 14 | 4-*n*-Pr($C_6H_4$) | Me | 5-F | 10 | **3n** | 93 |
| 15 | 4-*n*-Pr($C_6H_4$) | Me | 5-Cl | 10 | **3o** | 94 |
| 16 | 4-Cl($C_6H_4$) | Me | 5-F | 10 | **3p** | 90 |
| 17 | 4-Cl($C_6H_4$) | Me | 5-Cl | 10 | **3q** | 92 |

[a] Reaction conditions: **2** in $CH_2Cl_2$ (1.0 mL) was added to a solution of **1** and $Ph_3PAuNTf_2$ (2 mol%) using a syringe pump with addition over 2 h. After 1 h, $HCl_{concd}$ (40 μL, 2.4 equiv) was added.
[b] Yield of isolated product.
[c] DCE was used as the solvent and the reaction was carried out at 75 °C.

**Table 3** Control Reactions




**1a** (0.4 mmol) **2h** (1.2 equiv) **4h**, 79%




**4h** (0.2 mmol) **3h** **TsNH$_2$**

| Entry | Catalyst | Yield of **3h** (%) | Yield of **TsNH$_2$** (%) | Recovery of **4h** (%) |
|---|---|---|---|---|
| 1 | $Ph_3PAuNTf_2$ (2 mol%) $HCl_{concd}$ (40 μL) | 73 | 67 | 26 |
| 2 | $HCl_{concd}$ (40 μL) | 17 | – | 81 |
| 3 | $HNTf_2$ (4 mol%), $H_2O$ (40 μL) | 58 | 59 | 41 |
| 4 | $H_2O$ (40 μL) | – | – | 99 |

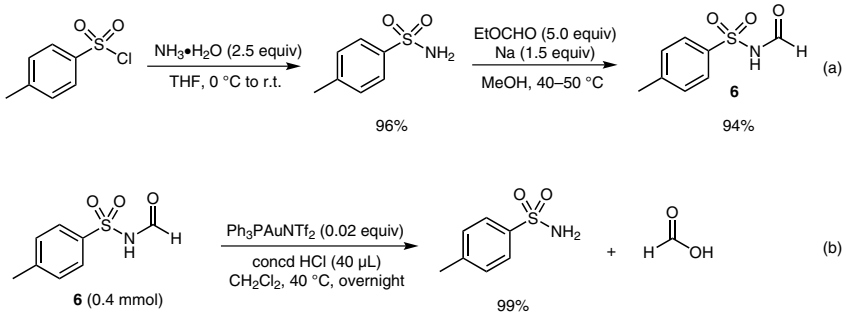
substituent on the benzene ring of the diazoindolinones **2** was examined. Compared to electron-donating groups (**3f**: $R^3$ = Me, 86%; **3g**: $R^3$ = MeO, 88%) (entries 6 and 7), electron-withdrawing substituents (such as, **3c**: $R^3$ = F, 99%; **3a**: $R^3$ = Cl, 95%) (entries 3 and 1) gave much better yields. However, with the stronger electron-withdrawing nitro group on the phenyl ring, the desired product **3b** was obtained in only 71% yield (entry 2). 5-Bromo-3-diazoindolin-2-one ($R^3$ = Br) gave the desired product **3d** in 87% yield (entry 4). Compound **3h** was obtained in only 71% yield (entry 8) due to steric effects. Subsequently, the $R^2$ substituents on the nitrogen of diazoindolinones **2** were explored. Electron-withdrawing groups such as 4-$NO_2$ and 4-Br on the phenyl ring were compatible in the reaction and desired products **3i** and **3j** (entries 9 and 10) were obtained in 78% and 85% yields, respectively. A 4-methylbenzyl or benzyl group on the nitrogen atom of **2** were also applicable, offering the target products with good yields (**3k**: 85%; **3l**: 74%) (entries 11 and 12). However, with an electron-withdrawing $R^2$ substituent (such as an acetyl group), no C=C cleavage product was detected. In addition, with poorly soluble N–H diazoindolinones, serious decomposition was observed and only trace amounts of the desired products were isolated. Finally, the effects of substituents on the carbonyl carbon of the enaminones ($R^1$) were investigated. An alkyl-substituted enaminone ($R^1$ = *t*-Bu) provided **3m** in 83% yield (entry 13). Aryl-substituted enaminones also tolerated the reaction conditions, affording products **3n–q** with excellent yields (90–94%) (entries 14–17).

To understand the reaction mechanism, several control experiments were conducted. When the reaction was carried out with **1a** and **2h** at room temperature in the presence of only Au(I), the C–H insertion product **4h** (*E*-isomer)[11a] was successfully isolated in a yield of 79% (Table 3). Other diazo compounds **2** were also used to prepare intermediates **4**, but all of them were easily converted into the final products **3** and the corresponding pure intermediates **4** were hard to isolate. Under the standard conditions, **4h** was transformed into product **3h** in 73% yield (Table 3, entry 1). This result suggested that **4h** was a possible intermediate. Treatment of **4h** with $HCl_{concd}$ (40 μL) gave **3h** in 17% yield after 48 hours (81% of **4h** recovered) (entry 2). When $H_2O$ (40 μL) and $HNTf_2$ (4 mol%) were used in place of $HCl_{concd}$ (40 μL), **3h** was obtained with an encouraging yield of 58% (entry 3). In the presence of $H_2O$ only, the C=C bond cleavage reaction did not occur (entry 4). These control experiments indicated that the reaction should be run in the presence of a gold catalyst, which might release the strong Brønsted acid $HNTf_2$.

Based on the experimental results and previously reported work,[11a] we have proposed a possible reaction mechanism (Scheme 2). Firstly, Au(I)-catalyzed decomposition of the diazo compound occurred (**2a** → **2a′**). Next, nucleophilic attack by the α-carbon of the enaminone **1a** (*Z*-isomer) on **2a′**, followed by a 1,2-H shift, provided the chemoselective C($sp^2$)-H functionalized intermediate **4a** (*E*-isomer). Subsequently, in the presence of the Brønsted acid, conjugate addition of $H_2O$ to **4a** occurred to furnish **5a**. Finally, cleavage of the carbon–carbon bond proceeded to form **3a** and the by-product **6** (CHONHTs).

However, compound **6** could not be detected in the reaction and only $TsNH_2$ was obtained. In order to clarify this result, compound **6** was prepared (Scheme 3, a)[15] and subjected to the standard reaction conditions. As expected, by-product **6** was converted into $TsNH_2$ quantitatively (Scheme 3, b).

To further clarify the reaction mechanism, ESI-MS analysis was performed during the reaction process (Scheme 2).[16] After the reaction (**1a** with **2a**, under the standard conditions) had progressed for 15 minutes, a sample was taken from the reaction mixture for ESI-MS analysis. Fortunately, the characteristic signal [**5a** + Na]$^+$ was observed. This high-resolution mass data of the detected complex was as follows: *m*/*z* [**5a** + Na]$^+$ calculated for $C_{25}H_{23}ClN_2NaO_5S$: 521.0908; found: 521.0916; with an error of –1.4 ppm, suggesting that **5a** was a possible intermediate in the formation of **3a**. Simultaneously, a characteristic signal [**6** + Na]$^+$ was also obtained (*m*/*z* [**6** + Na]$^+$ calculated for $C_8H_9NNaO_3S$: 222.0195; found: 222.0198; with an error of –1.0 ppm), which implies the presence of **6** during the reaction process, although so far it has not been isolated from the tan-



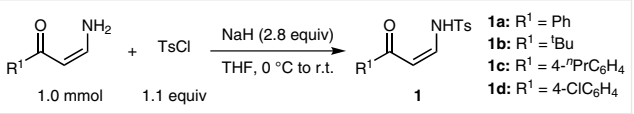

**Scheme 3** Preparation and hydrolysis of compound **6**

dem reaction. In addition, the characteristic signals for [**3a** + Na]$^+$ and [**4a** + Na]$^+$ were also observed. These ESI-MS data further support the possible reaction mechanism.

In conclusion, we have developed a novel one-pot reaction to synthesize 1-alkyl-3-(2-oxo-2-aryl/alkyl-ethyl)indolin-2-ones in good to excellent yields under mild reaction conditions. In this process, the Au(I)-catalyzed chemoselective C($sp^2$)–H functionalization of tosyl-substituted enaminones and Brønsted acid promoted selective cleavage of the carbon–carbon double bond are integrated effectively. The control experiments suggest that the cleavage process was promoted by the Brønsted acid and ESI-MS analysis further supports the proposed reaction mechanism. Further investigation of the reaction mechanism and the synthetic applications of the process are currently underway.

All reactions were performed in oven-dried glassware in air except when otherwise noted. The reactions were monitored by TLC carried out on Merck silica plates (silica gel 60 F254) using UV light for visualization. Starting materials and reagents were purchased from commercial suppliers (Acros, Sigma Aldrich and TCI Europe), which were used without further purification unless otherwise noted. Anhydrous $CH_2Cl_2$ and DCE were prepared by distillation from $CaH_2$. Column chromatographic purification of the products was carried out using Huanghai Chemical Co. Ltd. silica gel (300–400 mesh). IR spectra were recorded on a NICOLET iS50 FT-IR spectrophotometer. $^1$H and $^{13}$C NMR spectra were recorded at 400 MHz and 100 MHz, respectively, in $CDCl_3$ or DMSO-$d_6$ (containing 0.03% $Me_4Si$). $^1$H NMR spectra were recorded with $Me_4Si$ (δ = 0.00) as the internal reference and $^{13}$C NMR spectra were recorded with $CDCl_3$ (δ = 77.00) or DMSO-$d_6$ (δ = 39.52) as the internal reference. High-resolution mass spectra were obtained using a Bruker Maxis Impact mass spectrometer with a TOF (for EI or ESI) or FT-ICR (for MALDI) analyzer. Single-crystal X-ray diffraction data were collected on a Bruker SMARTAPEX diffractometer.

### Benzenesulfonamides 1; General Procedure (Scheme 4)




**Scheme 4**

Under an atmosphere of $N_2$, to a Schlenk tube were added $NH_2$-enaminone[13a] (1.0 mmol), TsCl (209.8 mg, 1.1 mmol) and anhydrous THF (15 mL) at 0 °C. After 20 min, NaH (60%, 112.0 mg, 2.8 mmol) was added in three portions over 0.5 h. The resulting mixture was stirred at 0 °C for about 0.5 h until the $NH_2$-enaminone had disappeared according to TLC analysis. The resulting mixture was quenched with sat. NaCl solution, and extracted with EtOAc (3 × 20 mL). The combined organic layers were dried over anhydrous $Na_2SO_4$, filtered and concentrated under reduced pressure. Purification of the residue by flash chromatography on silica gel ($CH_2Cl_2$–PE) afforded **1**.

Starting materials **1a**,**b**[17] are known compounds and the spectroscopic data are in agreement with those previously reported. The analytical data of products **1c**,**d** are as follows.

**(*Z*)-4-Methyl-*N*-[3-oxo-3-(4-propylphenyl)prop-1-en-1-yl]benzenesulfonamide (1c)**

White solid; yield: 199 mg (58%); mp 107–109 °C; $R_f$ = 0.32 ($CH_2Cl_2$–PE, 1:1).

IR (ATR): 2960, 2930, 1633, 1577, 1360, 1234, 1164, 1088, 1011, 915, 774, 735, 665 cm$^{-1}$.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 11.97 (d, *J* = 9.6 Hz, 1 H), 7.92–7.65 (m, 4 H), 7.33 (d, *J* = 8.0 Hz, 2 H), 7.28–7.21 (m, 3 H), 6.18 (d, *J* = 8.8 Hz, 1 H), 2.63 (t, *J* = 7.2 Hz, 2 H), 2.42 (s, 3 H), 1.70–1.60 (m, 2 H), 0.93 (t, *J* = 7.2 Hz, 3 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 192.5, 149.0, 145.0, 142.1, 137.5, 135.7, 130.4, 129.2, 128.3, 127.2, 99.6, 38.0, 24.1, 21.5, 13.6.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{19}H_{21}NNaO_3S$: 366.1134; found: 366.1136.

**(*Z*)-*N*-[3-(4-Chlorophenyl)-3-oxoprop-1-en-1-yl]-4-methylbenzenesulfonamide (1d)**

White solid; yield: 255 mg (76%); mp 146–148 °C; $R_f$ = 0.30 ($CH_2Cl_2$–PE, 1:1).

IR (ATR): 2960, 1634, 1575, 1360, 1236, 1165, 1088, 1006, 914, 772, 728, 663 cm$^{-1}$.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 11.88 (d, *J* = 10.0 Hz, 1 H), 7.90–7.65 (m, 4 H), 7.42 (d, *J* = 8.4 Hz, 2 H), 7.34 (d, *J* = 8.0 Hz, 2 H), 7.31–7.26 (m, 1 H), 6.14 (d, *J* = 8.8 Hz, 1 H), 2.43 (s, 3 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 191.4, 145.2, 142.9, 139.8, 137.3, 136.3, 130.5, 129.6, 129.4, 127.2, 99.0, 21.5.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{16}H_{14}ClNNaO_3S$: 358.0275; found: 358.0276.

### 1-Alkyl-3-(2-oxo-2-aryl/alkyl-ethyl)indolin-2-ones 3; General Procedure

Under an atmosphere of air, to a Schlenk tube were added enaminone **1** (0.20 mmol), $Ph_3PAuNTf_2$ (3.0 mg, 0.004 mmol) and anhydrous $CH_2Cl_2$ (2.5 mL). Next, diazooxindole **2** (0.24 mmol) in $CH_2Cl_2$ (1.0 mL) was added over 2 h using a syringe pump. The resulting mixture was stirred at ambient temperature for about 1 h until the enaminone **1** had disappeared by TLC analysis. $HCl_{concd}$ (40 μL) was added to the mixture which was kept stirring at 40 °C for the appropriate length of time (see Table 2). Subsequently, the reaction was cooled to r.t., PE (2 mL) was added and the mixture was directly subjected to column chromatography for purification.

**5-Chloro-1-methyl-3-(2-oxo-2-phenylethyl)indolin-2-one (3a)**

Yellowish solid; yield: 57 mg (95%); mp 103–105 °C; $R_f$ = 0.31 ($CH_2Cl_2$–PE, 4:1).

IR (ATR): 3059, 2905, 1709, 1683, 1610, 1489, 1344, 1223, 1099, 983, 809, 759, 733, 688 cm$^{-1}$.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 7.97 (d, *J* = 7.6 Hz, 2 H), 7.65–7.50 (m, 1 H), 7.50–7.38 (m, 2 H), 7.35–7.20 (m, 2 H), 6.77 (d, *J* = 8.8 Hz, 1 H), 4.10–3.90 (m, 1 H), 3.84 (dd, *J* = 18.4, 2.8 Hz, 1 H), 3.41 (dd, *J* = 18.4, 9.2 Hz, 1 H), 3.25 (s, 3 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 197.3, 177.7, 143.3, 136.4, 133.96, 131.0, 129.1, 128.5, 128.3, 128.2, 125.2, 109.1, 41.1, 39.8, 26.4.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{17}H_{14}ClNNaO_2$: 322.0605; found: 322.0613.

**1-Methyl-5-nitro-3-(2-oxo-2-phenylethyl)indolin-2-one (3b)**

Yellow solid; yield: 44 mg (71%); mp 153–155 °C; $R_f$ = 0.30 ($CH_2Cl_2$–EtOAc, 100:1).

IR (ATR): 3064, 2923, 1720, 1683, 1613, 1515, 1495, 1329, 1293, 1067, 752, 745, 690 $cm^{-1}$.

$^1H$ NMR (400 MHz, $CDCl_3$): δ = 8.27 (d, *J* = 8.4 Hz, 1 H), 8.11 (s, 1 H), 7.96 (d, *J* = 7.6 Hz, 2 H), 7.66–7.54 (m, 1 H), 7.54–7.40 (m, 2 H), 6.95 (d, *J* = 8.4 Hz, 1 H), 4.01 (d, *J* = 7.2 Hz, 1 H), 3.94 (dd, *J* = 18.8, 2.8 Hz, 1 H), 3.62 (dd, *J* = 18.4, 7.6 Hz, 1 H), 3.36 (s, 3 H).

$^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 196.6, 178.1, 150.5, 143.5, 136.0, 134.0, 129.8, 129.0, 128.4, 125.7, 119.9, 107.6, 40.8, 39.1, 26.6.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{17}H_{14}N_2NaO_4$: 333.0846; found: 333.0848.

**5-Fluoro-1-methyl-3-(2-oxo-2-phenylethyl)indolin-2-one (3c)**

White solid; yield: 56 mg (99%); mp 81–83 °C; $R_f$ = 0.32 ($CH_2Cl_2$–PE, 4:1).

IR (ATR): 3061, 2916, 1706, 1684, 1492, 1449, 1351, 1221, 1122, 895, 809, 768, 732, 688 $cm^{-1}$.

$^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 8.0 Hz, 2 H), 7.63–7.52 (m, 1 H), 7.51–7.35 (m, 2 H), 7.02 (d, *J* = 7.6 Hz, 1 H), 6.99–6.89 (m, 1 H), 6.81–6.68 (m, 1 H), 4.03 (d, *J* = 8.4 Hz, 1 H), 3.83 (dd, *J* = 18.4, 2.4 Hz, 1 H), 3.37 (dd, *J* = 18.4, 9.2 Hz, 1 H), 3.24 (s, 3 H).

$^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 197.4, 177.8, 159.6 (d, $J_{C-F}$ = 239.9 Hz), 140.7, 136.5, 133.9, 131.0 (d, $J_{C-F}$ = 8.7 Hz), 129.0, 128.4, 114.4 (d, $J_{C-F}$ = 23.5 Hz), 113.0 (d, $J_{C-F}$ = 25.2 Hz), 108.5 (d, $J_{C-F}$ = 8.2 Hz), 41.4, 39.8, 26.4.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{17}H_{14}FNNaO_2$: 306.0901; found: 306.0905.

**5-Bromo-1-methyl-3-(2-oxo-2-phenylethyl)indolin-2-one (3d)**

Yellowish solid; yield: 60 mg (87%); mp 138–140 °C; $R_f$ = 0.32 ($CH_2Cl_2$–PE, 4:1).

IR (ATR): 3060, 2915, 1708, 1683, 1607, 1488, 1343, 1223, 1097, 808, 759, 734, 689 $cm^{-1}$.

$^1H$ NMR (400 MHz, $CDCl_3$): δ = 8.10–7.92 (m, 2 H), 7.65–7.55 (m, 1 H), 7.52–7.45 (m, 2 H), 7.44–7.35 (m, 2 H), 6.74 (d, *J* = 8.0 Hz, 1 H), 4.04 (dd, *J* = 8.8, 2.8 Hz, 1 H), 3.85 (dd, *J* = 18.4, 3.2 Hz, 1 H), 3.42 (dd, *J* = 18.4, 9.2 Hz, 1 H), 3.25 (s, 3 H).

$^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 197.2, 177.7, 143.9, 136.5, 134.0, 131.5, 131.3, 129.1, 128.5, 128.0, 115.5, 109.7, 41.1, 39.8, 26.4.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{17}H_{14}BrNNaO_2$: 366.0100; found: 366.0110.

**1-Methyl-3-(2-oxo-2-phenylethyl)indolin-2-one (3e)**

Yellowish solid; yield: 42 mg (82%); mp 107–109 °C; $R_f$ = 0.30 ($CH_2Cl_2$–PE, 4:1).

IR (ATR): 3055, 2916, 1705, 1686, 1470, 1347, 1265, 1223, 1088, 731, 701, 689 $cm^{-1}$.

$^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.98 (d, *J* = 7.6 Hz, 2 H), 7.63–7.54 (m, 1 H), 7.52–7.41 (m, 2 H), 7.34–7.20 (m, 2 H), 7.05–6.95 (m, 1 H), 6.86 (d, *J* = 7.6 Hz, 1 H), 4.08 (d, *J* = 8.0 Hz, 1 H), 3.90–3.75 (m, 1 H), 3.39 (dd, *J* = 18.0, 9.2 Hz, 1 H), 3.27 (s, 3 H).

$^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 197.6, 178.3, 144.7, 136.7, 133.8, 129.5, 129.0, 128.5, 128.4, 124.7, 122.8, 108.3, 41.1, 40.0, 26.3.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{17}H_{15}NNaO_2$: 288.0995; found: 288.1001.

**1,5-Dimethyl-3-(2-oxo-2-phenylethyl)indolin-2-one (3f)**

Yellowish solid; yield: 48 mg (86%); mp 117–119 °C; $R_f$ = 0.33 ($CH_2Cl_2$–PE, 4:1).

IR (ATR): 2916, 1702, 1684, 1578, 1497, 1349, 1223, 1092, 986, 807, 767, 731, 687 $cm^{-1}$.

$^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.99 (d, *J* = 7.6 Hz, 2 H), 7.64–7.53 (m, 1 H), 7.51–7.42 (m, 2 H), 7.07 (br s, 2 H), 6.75 (d, *J* = 8.4 Hz, 1 H), 4.06 (d, *J* = 8.0 Hz, 1 H), 3.83 (dd, *J* = 18.4, 2.8 Hz, 1 H), 3.38 (dd, *J* = 18.4, 9.6 Hz, 1 H), 3.25 (s, 3 H), 2.28 (s, 3 H).

$^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 197.7, 178.2, 142.3, 136.7, 133.8, 132.4, 129.5, 129.0, 128.6, 128.5, 125.6, 108.0, 41.1, 40.1, 26.3, 20.9.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{18}H_{17}NNaO_2$: 302.1151; found: 302.1158.

**5-Methoxy-1-methyl-3-(2-oxo-2-phenylethyl)indolin-2-one (3g)**

White solid; yield: 52 mg (88%); mp 114–116 °C; $R_f$ = 0.28 ($CH_2Cl_2$–EtOAc, 60:1).

IR (ATR): 3256, 3065, 1683, 1598, 1497, 1334, 1294, 1158, 1030, 814, 767, 688, 665 $cm^{-1}$.

$^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.97 (d, *J* = 7.6 Hz, 2 H), 7.63–7.52 (m, 1 H), 7.52–7.41 (m, 2 H), 6.89 (s, 1 H), 6.83–6.72 (m, 2 H), 4.04 (d, *J* = 7.2 Hz, 1 H), 3.82 (dd, *J* = 18.4, 2.8 Hz, 1 H), 3.73 (s, 3 H), 3.39 (dd, *J* = 18.4, 9.2 Hz, 1 H), 3.24 (s, 3 H).

$^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 197.6, 177.8, 156.3, 138.1, 136.5, 133.7, 130.6, 128.9, 128.3, 112.5, 112.1, 108.4, 55.7, 41.4, 39.9, 26.2.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{18}H_{17}NNaO_3$: 318.1101; found: 318.1101.

**4,6-Dichloro-1-methyl-3-(2-oxo-2-phenylethyl)indolin-2-one (3h)**

White solid; yield: 48 mg (71%); mp 138–140 °C; $R_f$ = 0.30 ($CH_2Cl_2$–PE, 3:1).

IR (ATR): 3063, 1720, 1685, 1606, 1580, 1347, 1290, 1213, 1080, 1022, 972, 835, 735, 720, 689 $cm^{-1}$.

$^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.90 (d, *J* = 7.6 Hz, 2 H), 7.65–7.50 (m, 1 H), 7.50–7.35 (m, 2 H), 6.95 (d, *J* = 1.2 Hz, 1 H), 6.80 (d, *J* = 1.2 Hz, 1 H), 4.26 (dd, *J* = 19.2, 5.2 Hz, 1 H), 3.90–3.40 (m, 2 H), 3.29 (s, 3 H).

$^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 196.9, 177.3, 147.7, 136.3, 134.9, 133.9, 130.4, 129.0, 128.4, 124.4, 122.6, 107.8, 41.5, 36.9, 26.7.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{17}H_{13}Cl_2NNaO$: 356.0216; found: 356.0222.

**5-Chloro-1-(4-nitrobenzyl)-3-(2-oxo-2-phenylethyl)indolin-2-one (3i)**

Yellowish solid; yield: 66 mg (78%); mp 200–202 °C; $R_f$ = 0.30 ($CH_2Cl_2$–PE, 8:1).

IR (ATR): 3065, 1713, 1685, 1609, 1519, 1485, 1342, 1218, 1163, 812, 736, 689 $cm^{-1}$.

$^1H$ NMR (400 MHz, DMSO-$d_6$): δ = 8.23 (d, *J* = 8.4 Hz, 2 H), 8.02 (d, *J* = 7.2 Hz, 2 H), 7.75–7.63 (m, 3 H), 7.59–7.48 (m, 2 H), 7.44 (s, 1 H), 7.23 (d, *J* = 7.2 Hz, 1 H), 6.86 (d, *J* = 8.0 Hz, 1 H), 5.25–5.00 (m, 2 H), 4.25–4.00 (m, 2 H), 3.85 (dd, *J* = 18.8, 5.2 Hz, 1 H).

$^{13}C$ NMR (100 MHz, DMSO-$d_6$): δ = 197.9, 177.6, 147.4, 144.8, 142.6, 136.3, 134.1, 131.8, 129.2, 128.8, 128.6, 127.6, 126.6, 124.1, 124.0, 110.2, 42.4, 41.0, 38.0.

HRMS (ESI): $m/z$ [M + Na]$^+$ calcd for $C_{23}H_{17}ClN_2NaO_4$: 443.0769; found: 443.0772.

**1-(4-Bromobenzyl)-5-chloro-3-(2-oxo-2-phenylethyl)indolin-2-one (3j)**

Yellowish solid; yield: 77 mg (85%); mp 223–225 °C; $R_f$ = 0.26 ($CH_2Cl_2$–PE, 1:1).

IR (ATR): 3063, 1712, 1686, 1611, 1485, 1362, 1220, 812, 800, 752, 684 cm$^{-1}$.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 7.99 (d, $J$ = 7.6 Hz, 2 H), 7.62–7.56 (m, 1 H), 7.55–7.43 (m, 4 H), 7.26–7.20 (m, 3 H), 7.13 (d, $J$ = 8.0 Hz, 1 H), 6.60 (d, $J$ = 8.4 Hz, 1 H), 5.10–4.80 (m, 2 H), 4.08 (d, $J$ = 6.4 Hz, 1 H), 3.90 (dd, $J$ = 18.4, 2.8 Hz, 1 H), 3.55 (dd, $J$ = 18.4, 8.0 Hz, 1 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 197.0, 177.9, 142.2, 136.4, 134.9, 134.1, 132.4, 131.0, 129.4, 129.2, 128.6, 128.5, 128.3, 125.2, 122.1, 110.1, 43.5, 41.3, 39.6.

HRMS (ESI): $m/z$ [M + Na]$^+$ calcd for $C_{23}H_{17}BrClNNaO_2$: 476.0023; found: 476.0024.

**1-Benzyl-5-chloro-3-(2-oxo-2-phenylethyl)indolin-2-one (3k)**

White solid; yield: 64 mg (85%); mp 182–184 °C; $R_f$ = 0.30 ($CH_2Cl_2$–PE, 3:2).

IR (ATR): 2915, 1708, 1688, 1610, 1487, 1350, 1220, 1178, 801, 754, 740, 723, 699, 687 cm$^{-1}$.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 8.05–7.96 (m, 2 H), 7.65–7.56 (m, 1 H), 7.54–7.45 (m, 2 H), 7.37–7.32 (m, 4 H), 7.32–7.27 (m, 1 H), 7.26–7.22 (m, 1 H), 7.12 (dd, $J$ = 8.4, 2.0 Hz, 1 H), 6.64 (d, $J$ = 8.4 Hz, 1 H), 4.97 (s, 2 H), 4.13 (dd, $J$ = 8.8, 2.8 Hz, 1 H), 3.91 (dd, $J$ = 18.4, 2.8 Hz, 1 H), 3.51 (dd, $J$ = 18.4, 8.8 Hz, 1 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 197.1, 177.9, 142.4, 136.5, 135.9, 134.0, 131.1, 129.2, 129.1, 128.6, 128.32, 128.28, 128.1, 127.6, 125.2, 110.2, 44.1, 41.2, 39.8.

HRMS (ESI): $m/z$ [M + Na]$^+$ calcd for $C_{23}H_{18}ClNNaO_2$: 398.0918; found: 398.0920.

**5-Chloro-1-(4-methylbenzyl)-3-(2-oxo-2-phenylethyl)indolin-2-one (3l)**

White solid; yield: 58 mg (74%); mp 206–208 °C; $R_f$ = 0.30 ($CH_2Cl_2$–PE, 4:1).

IR (ATR): 3063, 1716, 1670, 1486, 1363, 1219, 803, 757, 686 cm$^{-1}$.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 8.00 (d, $J$ = 7.6 Hz, 2 H), 7.65–7.55 (m, 1 H), 7.54–7.35 (m, 2 H), 7.25–7.17 (m, 3 H), 7.16–7.08 (m, 3 H), 6.65 (d, $J$ = 8.4 Hz, 1 H), 4.92 (s, 2 H), 4.12 (dd, $J$ = 8.4, 2.4 Hz, 1 H), 3.90 (dd, $J$ = 18.4, 2.8 Hz, 1 H), 3.48 (dd, $J$ = 18.8, 9.2 Hz, 1 H), 2.33 (s, 3 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 197.2, 177.9, 142.5, 137.9, 136.5, 134.0, 132.8, 131.1, 129.9, 129.1, 128.6, 128.3, 127.7, 125.2, 110.3, 43.8, 41.2, 39.9, 21.0.

HRMS (ESI): $m/z$ [M + Na]$^+$ calcd for $C_{24}H_{20}ClNNaO_2$: 412.1075; found: 412.1086.

**5-Chloro-3-(3,3-dimethyl-2-oxobutyl)-1-methylindolin-2-one (3m)**

Yellow oil; yield: 46 mg (83%); $R_f$ = 0.33 ($CH_2Cl_2$–PE, 3:1).

IR (ATR): 2968, 1703, 1610, 1490, 1343, 1101, 1070, 811, 735, 656 cm$^{-1}$.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 7.17 (d, $J$ = 8.0 Hz, 1 H), 7.04 (s, 1 H), 6.68 (d, $J$ = 8.4 Hz, 1 H), 3.76 (d, $J$ = 6.8 Hz, 1 H), 3.25 (dd, $J$ = 18.8, 2.8 Hz, 1 H), 3.15 (s, 3 H), 2.89 (dd, $J$ = 18.4, 8.8 Hz, 1 H), 1.10 (s, 9 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 213.6, 177.9, 143.4, 131.1, 128.3, 128.2, 124.7, 109.1, 43.9, 41.1, 38.0, 26.3.

HRMS (ESI): $m/z$ [M + Na]$^+$ calcd for $C_{15}H_{18}ClNNaO_2$: 302.0918; found: 302.0910.

**5-Fluoro-1-methyl-3-[2-oxo-2-(4-propylphenyl)ethyl]indolin-2-one (3n)**

Yellowish solid, yield: 60 mg (93%); mp 71–73 °C; $R_f$ = 0.35 ($CH_2Cl_2$).

IR (ATR): 2959, 1708, 1680, 1606, 1492, 1350, 1224, 1121, 988, 805, 735, 689 cm$^{-1}$.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 7.89 (d, $J$ = 7.6 Hz, 2 H), 7.27 (d, $J$ = 7.6 Hz, 2 H), 7.08–7.00 (m, 1 H), 7.00–6.90 (m, 1 H), 6.76 (dd, $J$ = 8.4, 4.0 Hz, 1 H), 4.04 (d, $J$ = 8.0 Hz, 1 H), 3.82 (ddd, $J$ = 18.4, 2.8, 0.8 Hz, 1 H), 3.36 (ddd, $J$ = 18.0, 9.2, 0.8 Hz, 1 H), 3.25 (s, 3 H), 2.64 (t, $J$ = 7.6 Hz, 2 H), 1.75–1.60 (m, 2 H), 0.93 (td, $J$ = 7.2, 0.8 Hz, 3 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 197.0, 177.9, 159.6 (d, $J_{C-F}$ = 239.9 Hz), 149.5, 140.6 (d, $J_{C-F}$ = 1.9 Hz), 134.2, 131.1 (d, $J_{C-F}$ = 8.7 Hz), 129.1, 128.6, 114.4 (d, $J_{C-F}$ = 23.4 Hz), 113.1 (d, $J_{C-F}$ = 25.2 Hz), 108.5 (d, $J_{C-F}$ = 8.3 Hz), 41.5, 39.7, 37.9, 26.3, 24.0, 13.5.

HRMS (ESI): $m/z$ [M + Na]$^+$ calcd for $C_{20}H_{20}FNNaO_2$: 348.1370; found: 348.1376.

**5-Chloro-1-methyl-3-[2-oxo-2-(4-propylphenyl)ethyl]indolin-2-one (3o)**

Yellowish solid, yield: 64 mg (94%); mp 101–103 °C; $R_f$ = 0.35 ($CH_2Cl_2$).

IR (ATR): 2959, 1710, 1680, 1607, 1490, 1343, 1100, 986, 807, 735, 705 cm$^{-1}$.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 7.89 (d, $J$ = 8.0 Hz, 2 H), 7.40–7.20 (m, 4 H), 6.77 (d, $J$ = 8.8 Hz, 1 H), 4.03 (d, $J$ = 7.6 Hz, 1 H), 3.82 (dd, $J$ = 18.4, 2.4 Hz, 1 H), 3.39 (dd, $J$ = 18.4, 9.2 Hz, 1 H), 3.26 (s, 3 H), 2.64 (t, $J$ = 7.6 Hz, 2 H), 1.70–1.60 (m, 2 H), 0.94 (t, $J$ = 7.2 Hz, 3 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 196.9, 177.9, 149.6, 143.3, 134.3, 131.2, 129.2, 128.6, 128.3, 128.2, 125.3, 109.1, 41.2, 39.7, 38.0, 26.4, 24.0, 13.6.

HRMS (ESI): $m/z$ [M + Na]$^+$ calcd for $C_{20}H_{20}ClNNaO_2$: 364.1075; found: 364.1075.

**3-[2-(4-chlorophenyl)-2-oxoethyl]-5-fluoro-1-methylindolin-2-one (3p)**

White solid, yield: 57 mg (90%); mp 139–141 °C; $R_f$ = 0.35 ($CH_2Cl_2$).

IR (ATR): 2905, 1708, 1686, 1589, 1493, 1352, 1221, 1092, 987, 819, 688 cm$^{-1}$.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 8.00–7.85 (m, 2 H), 7.55–7.40 (m, 2 H), 7.06–6.92 (m, 2 H), 6.77 (dd, $J$ = 8.4, 4.0 Hz, 1 H), 4.03 (dd, $J$ = 9.2, 2.4 Hz, 1 H), 3.81 (dd, $J$ = 18.4, 3.2 Hz, 1 H), 3.35 (dd, $J$ = 18.4, 9.2 Hz, 1 H), 3.26 (s, 3 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 196.2, 177.7, 159.7 (d, $J_{C-F}$ = 239.9 Hz), 140.7 (d, $J_{C-F}$ =2.0 Hz), 140.5, 134.8, 130.8 (d, $J_{C-F}$ = 8.7 Hz), 129.9, 129.4, 114.6 (d, $J_{C-F}$ = 23.5 Hz), 113.1 (d, $J_{C-F}$ = 25.2 Hz), 108.7 (d, $J_{C-F}$ = 8.2 Hz), 41.4, 39.9, 26.4.

HRMS (ESI): $m/z$ [M + Na]$^+$ calcd for $C_{17}H_{13}FClNNaO_2$: 340.0511; found: 340.0515.

**5-Chloro-3-[2-(4-chlorophenyl)-2-oxoethyl]-1-methylindolin-2-one (3q)**

Yellowish solid, yield: 61 mg (92%); mp 149–151 °C; $R_f$ = 0.35 ($CH_2Cl_2$).

IR (ATR): 2907, 1709, 1684, 1588, 1489, 1344, 1221, 1092, 986, 812, 736, 651 $cm^{-1}$.

$^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.91 (d, *J* = 8.4 Hz, 2 H), 7.45 (d, *J* = 8.4 Hz, 2 H), 7.35–7.15 (m, 2 H), 6.78 (d, *J* = 8.0 Hz, 1 H), 4.02 (d, *J* = 7.2 Hz, 1 H), 3.81 (dd, *J* = 18.4, 2.4 Hz, 1 H), 3.38 (dd, *J* = 18.4, 8.8 Hz, 1 H), 3.26 (s, 3 H).

$^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 196.1, 177.6, 143.4, 140.6, 134.8, 130.9, 129.9, 129.5, 128.5, 128.3, 125.2, 109.2, 41.1, 39.8, 26.4.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{17}H_{13}Cl_2NNaO_2$: 356.0216; found: 356.0217.

**(*E*)-*N*-[2-(4,6-Dichloro-1-methyl-2-oxoindolin-3-yl)-3-oxo-3-phenylprop-1-en-1-yl]-4-methylbenzenesulfonamide (4h)**

In air, to a Schlenk tube were added enaminone **1a** (120.6 mg, 0.40 mmol), $Ph_3PAuNTf_2$ (5.9 mg, 0.008 mmol) and anhydrous $CH_2Cl_2$ (5 mL). Next, diazooxindole **2h** (116.2 mg, 0.48 mmol) in $CH_2Cl_2$ (3.0 mL) was added over 3 h using a syringe pump. The resulting mixture was stirred at ambient temperature for 0.5 h until enaminone **1a** had disappeared according to TLC analysis. Subsequently, the mixture was subjected to flash column chromatography for purification directly, using $CH_2Cl_2$–acetone (15:0 to 15:1, v/v) as the eluent.

Yellowish solid, yield: 163 mg (79%); mp 125–127 °C; $R_f$ = 0.26 ($CH_2Cl_2$–acetone, 15:1).

IR (ATR): 3175, 3061, 1719, 1701, 1607, 1349, 1267, 1089, 873, 840, 746, 718, 703, 670 $cm^{-1}$.

$^1H$ NMR (400 MHz, DMSO-$d_6$): δ = 11.84 (br s, 1 H), 7.73 (d, *J* = 8.0 Hz, 2 H), 7.63–7.55 (m, 1 H), 7.55–7.44 (m, 4 H), 7.40–7.30 (m, 3 H), 7.17 (s, 1 H), 7.04 (s, 1 H), 4.87 (s, 1 H), 3.18 (s, 3 H), 2.44 (s, 3 H).

$^{13}C$ NMR (100 MHz, DMSO-$d_6$): δ = 194.3, 174.8, 148.0, 145.1, 138.2, 137.3, 133.8, 132.2, 130.7, 129.2, 129.0, 128.9, 126.8, 124.3, 121.5, 114.8, 108.2, 43.2, 26.8, 21.0.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{25}H_{20}Cl_2N_2NaO_4S$: 537.0413; found: 537.0417.

**4-Methylbenzenesulfonamide ($TsNH_2$);[18] Hydrolysis of Compound 6**

In air, to a Schlenk tube were added compound **6** (79.7 mg, 0.40 mmol),[15] $Ph_3PAuNTf_2$ (5.9 mg, 0.02 equiv), anhydrous $CH_2Cl_2$ (6 mL) and $HCl_{concd}$ (12 M, 40 µL, 2.4 equiv). The resulting mixture was stirred at 40 °C overnight (about 10 h). Subsequently, the reaction was cooled to r.t., and the mixture was subjected to flash column chromatography for purification directly, using $CH_2Cl_2$–EtOAc as the eluent.

White solid, yield: 67.6 mg (99%); $R_f$ = 0.28 ($CH_2Cl_2$–EtOAc, 60:1).

IR (ATR): 3355, 3260, 1529, 1301, 1160, 1098, 905, 817, 704 $cm^{-1}$.

$^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.82 (d, *J* = 7.6 Hz, 2 H), 7.31 (d, *J* = 8.0 Hz, 2 H), 4.98 (s, 2 H), 2.43 (s, 3 H).

$^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 143.9, 139.4, 129.9, 126.7, 21.2.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_7H_9NNaO_2S$: 194.0246; found: 194.0243.

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## Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0036-1588820.

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