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Diastereoselective synthesis of *trans*-2,3-dihydroindoles *via* formal [4 + 1] annulation reactions of a sulfonium ylide†

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We have established an *in situ* generated sulfonium-ylide mediated annulation to construct 2,3-di-substituted-2,3-dihydroindoles. The [4 + 1] annulation approach relied on Michael addition/substitution reactions. These reactions were carried out at ambient temperature to deliver dihydroindoles with excellent yields and diastereoselectivities. Moreover, the versatility of this approach allows for the introduction of various functional groups, enabling further diversification of the dihydroindoles. Also, the cascade approach was broadened to synthesize dihydrobenzofurans.

Introduction

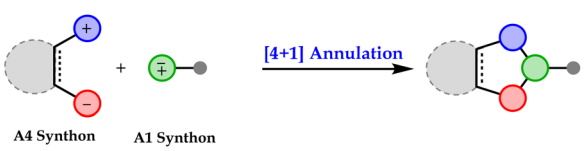
[4 + 1] Annulation is an effective technique that enables the construction of diversely substituted five-membered rings in a one-pot operation.[1–4] It is successfully mediated by a number of combinations of A4- and A1-synthons (Scheme 1), which produce a variety of five-membered heterocyclic compounds, including fused and spirocyclic frameworks.[1–4] Various Michael acceptors, including conjugated carbonyl compounds, conjugated imines, azoalkenes, and many more, often serve as A4-synthons in [4 + 1] annulation reactions.[5,6] Besides a variety of A1-synthons,[7–9] ylides are one of the most powerful and versatile synthons in synthetic organic chemistry, offering a wide range of reactivity patterns and functional group compatibility.[10,11] Consequently, they hold great potential for synthesizing complex natural and biologically active compounds.[12] They have both electrophilic and nucleophilic centers localized on the same carbon atom. Among the manifold applications of ylides, their participation in formal [4 + 1] annulation reactions stands out as the most prominent and promising area of research. Several cascade approaches have been established utilizing ylide chemistry to access N-heterocycles with remarkable efficiency and selectivity.[10,11,13–18]

N-heterocycles have significant importance in medicinal chemistry, drug discovery, and the synthesis of natural products.[19–21] In particular, 2,3-disubstituted dihydroindoles (DHIs) play key roles in the development of new pharmacological drugs. DHIs are prevalent in various bioactive compounds and alkaloids, *e.g.*, vindoline,[22] aspidospermidine,[23] strychnine,[24] flustramine B,[25] physostigmine,[26] and WAY-163909 [27] (Fig. 1).

The majorly reported strategy for the synthesis of DHIs is reduction of indoles *via* catalytic hydrogenation or dearomative annulation.[28,29] In the last decade, synthetic techniques for dihydroindoles have expanded to other organo- as well as metal-catalysed approaches.[30–33] Recently, our group has demonstrated a supported pyridinium ylide-mediated cascade synthesis of *trans*-2,3-dihydroindoles[34] and *trans*-2,3-dihydrobenzofurans.[35] In continuation of our study, we hypothesized that a sulfonium salt would participate in the *in situ* generation of a sulfonium ylide. This sulfonium ylide might then undergo a 1,4-conjugate addition with an *ortho*-aminochalcone followed by subsequent cyclization through *N*-substitution, yielding the corresponding DHIs.

Results and discussion

At the outset, an experiment was conducted wherein a reaction was performed using phenacyl sulfonium salt **1a** and *ortho*-aminochalcone **2aa** in the presence of triethylamine as a base



Scheme 1 General strategy of the [4 + 1] annulation.

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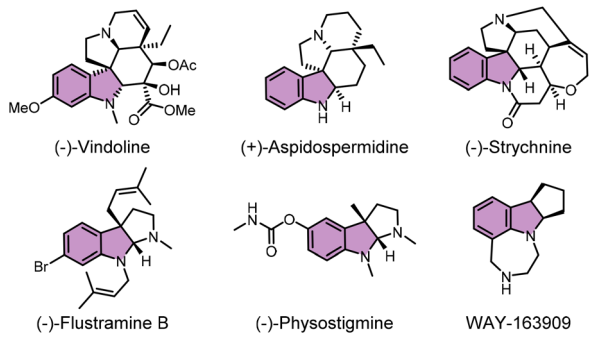
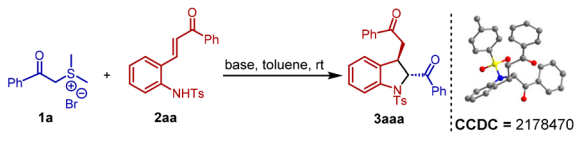


Fig. 1 Selected examples of bioactive indolines.

at ambient temperature in toluene. Pleasingly, the cascade reaction led to 2,3-disubstituted dihydroindole **3aaa** in a viable yield (Table 1, entry 1). The structure of product **3aaa** as a *trans*-isomer was confirmed by single crystal X-ray analysis.

Next, we conducted a systematic investigation of several organic and inorganic bases and solvents to determine the optimal reaction conditions for this cascade approach. Almost a similar outcome was observed with *N*-ethyl diisopropylamine as the base (Table 1, entry 2). When the reaction was carried out with stronger bases, namely 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), significant reduction in the reaction time was observed (Table 1, entries 3 and 4). However, the yield of the desired product was unaltered. A slight increment in the yield was noted with *N*-methyl pyrrolidine (NMP) and *N*-methyl piperidine (NMPPR) (Table 1, entries 5 and 6). The yield of product **3aaa** was drastically decreased with the inorganic base sodium carbonate (Table 1, entry 7). Notably, cesium carbonate was identified as an appropriate base in terms of yield and time. Subsequently, several solvents were evaluated (Table 2). Eventually, toluene emerged as the most favourable solvent for this cascade

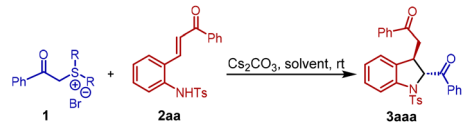
Table 1 Optimization of the cascade reaction conditions with different bases



Entry	Base (1 equiv.)	Time (h)	Yield (%)
1	Et_3N	48	82
2	$^iPr_2NEt$	48	80
3	DBU	24	84
4	DBN	26	82
5	NMP	30	86
6	NMPPR	34	81
7	Na_2CO_3	48	40
8	K_2CO_3	32	92
9	Cs_2CO_3	24	97

Reaction conditions: **1a** (0.3 mmol), **2aa** (0.2 mmol), base (0.2 mmol), and toluene (2 mL), unless specified. Diastereoisomeric ratios for all entries (>99 : 1) were determined by ^{1}H-NMR analysis.

Table 2 Effect of solvents



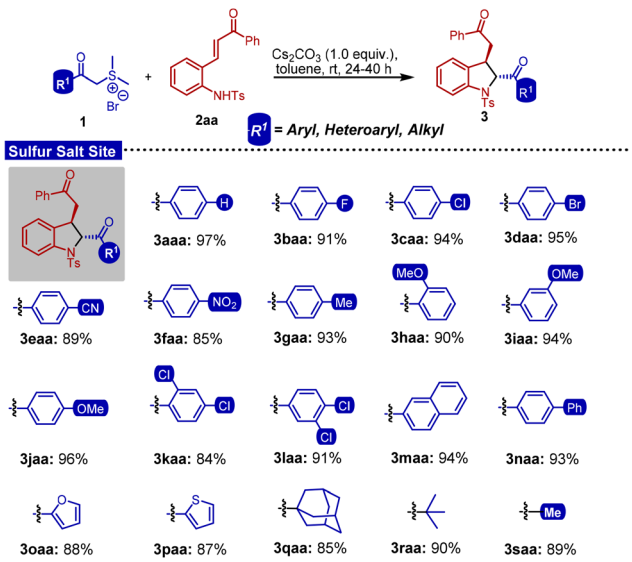
Entry	Solvent	R	Time (h)	Yield (%)
1	Toluene	Me	24	97
2	CH_3CN	Me	24	80
3	CH_2Cl_2	Me	32	85
4	EtOAc	Me	28	89
5	THF	Me	38	75
6[a]	H_2O	Me	48	41
7	Toluene	$-CH_2(CH_2)_2CH_2-$	28	94
8	Toluene	$-CH(CH)_2CH-$	28	92

Reaction conditions: **1** (0.3 mmol), **2aa** (0.2 mmol), Cs_2CO_3 (0.2 mmol), and solvent (2 mL), unless specified. Diastereoisomeric ratios for all entries (>99 : 1) were determined by ^{1}H-NMR analysis. [a] dr = 20 : 1.

approach. To further check the reactivity and selectivity of the reaction, we explored the cyclic sulfonium salt of phenacyl bromide (Table 2, entries 7 and 8). Remarkably, the cascade reaction proceeded smoothly, albeit with a slight reduction in the yield. After thorough evaluation, the dimethyl sulfonium salt **1a** was identified as the optimal A1-synthon for this cascade approach, offering maximum efficiency.

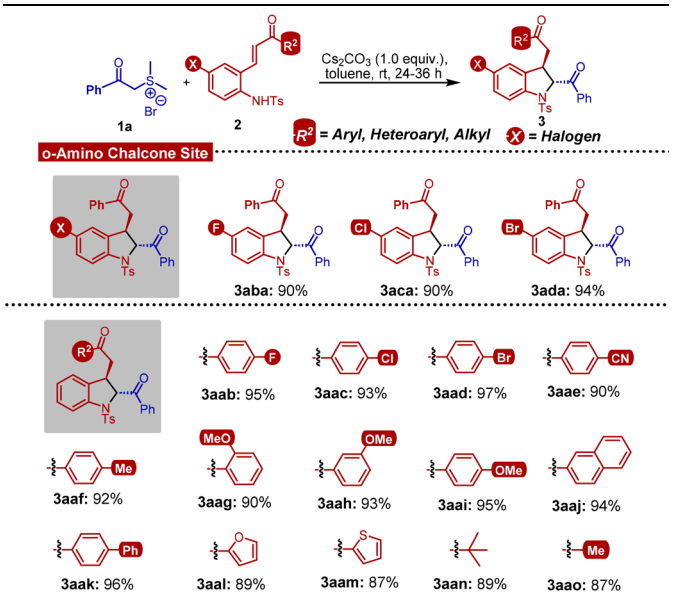
Having established the optimal reaction conditions, we explored the substrate generality of this [4 + 1] annulation reaction (Tables 3 and 4). At first, we examined the effect of the substitution pattern on the phenacyl sulfonium salt (Table 3). Specifically, we investigated the effects of introducing halogens

Table 3 Substrate scope of sulfonium salts



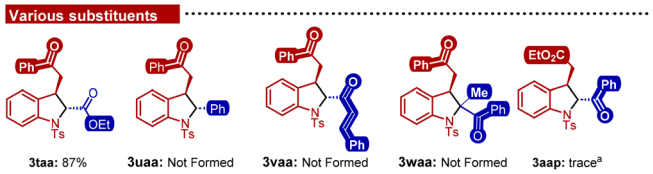
Reaction conditions: **1** (0.3 mmol), **2aa** (0.2 mmol), Cs_2CO_3 (0.2 mmol), and toluene (2 mL), unless specified. Diastereoisomeric ratios for all entries (>99 : 1) were determined by ^{1}H-NMR analysis.

Table 4 Substrate scope of *ortho*-aminochalcones



Reaction conditions: **1a** (0.3 mmol), **2** (0.2 mmol), Cs_2CO_3 (0.2 mmol), and toluene (2 mL), unless specified. Diastereoisomeric ratios for all entries (>99 : 1) were determined by ^{1}H-NMR analysis.

Table 5 Substrate scope



Reaction conditions: **1** (0.3 mmol), **2** (0.2 mmol), Cs_2CO_3 (0.2 mmol), and toluene (2 mL), unless specified. [a] The reaction was conducted at 80 °C and the formation of a trace amount of the product was confirmed by HRMS analysis and ^{1}H NMR of the crude reaction mixture.

(**1b–d**) (fluoro, chloro, and bromo), electron-withdrawing groups (**1e** and **1f**) (cyano and nitro), and the methyl group **1g** at the *para*-position of the aryl ring of compound **1**. Remarkably, all of these led to the corresponding DHIs (**3baa–gaa**) in excellent yields.

The introduction of an electron-donating group, specifically methoxy (**1h–j**), at the *ortho*-, *meta*- and *para*-positions of the aryl ring was observed to be well tolerated under the optimized conditions. Excellent yields were observed when dichloro-substitution was introduced at both the 2,5- and 3,4-positions (**1k** and **1l**) of the aryl ring in sulfonium salt **1**. Importantly, 2-naphthyl (**1m**) and biphenyl (**1n**) substituted sulfonium salts also resulted in the formation of the corresponding DHIs (**3maa** and **3naa**) in excellent yields. Additionally, we discovered that sterically and electronically diverse R^1 groups, including heterocycles (**1o** and **1p**) *i.e.*, 2-furyl and 2-thiophenyl, and aliphatic groups (**1q–s**) *i.e.*, adamantyl, *tert*-butyl, and methyl, were also well suited for the reaction and successfully transformed into the desired dihydroindoles. Next, our investigation focused on elucidating the effect of substitution on *ortho*-aminochalcones **2** (Table 4). To begin with, the influence of halogens on the 5-position of the aryl ring was investigated and fluoro, chloro, and bromo substituted DHIs were constructed (**3aba–3ada**). To further expand the scope of the [4 + 1] annulation reaction, we varied the R^2 group of *ortho*-aminochalcone **2**. For instance, halogen, cyano, and methyl were strategically introduced at the *para*-positions of the aryl ring of compound **2**. Remarkably, all of these substitutions were well tolerated. Amenable outcomes were obtained when the R^2 group was represented by differently substituted methoxy groups on the aryl ring. Additionally, a favourable outcome was observed with R^2 groups as 2-naphthyl, biphenyl, heteroaryl, and alkyl. Notably, it was seen that all the dihydroindoles were obtained exclusively as a single *trans*-isomer.

Furthermore, we explored various sulfonium salt derivatives (**1t–1v**) including secondary sulfonium salt **1w** (Table 5). Among them, ester-derived sulfonium salt **1t** was found to be efficient, leading to dihydroindole **3taa**. However, the cascade reaction with other salts (**1u–1w**) did not yield the anticipated products. Next, the reaction with the electronically distinct *ortho*-aminochalcone bearing ester functionality **2ap** provided a trace amount of the corresponding DHI at elevated temperatures.

Drawing upon insights from the previous reports,[34,35] a plausible mechanism for this [4 + 1] annulation reaction was proposed, as shown in Fig. 2. The cascade reaction is initiated with base promoted *in situ* generation of a sulfonium ylide, which functioned as the active A1 synthon. The *in situ* generated sulfonium ylide then reacts with aminochalcone **2** in a conjugate addition fashion, forming intermediate **A**. Notably, the sulfonium ylide can also be prepared and later used in the cascade reaction with or without any base to provide the same products (Table 6). This suggests that the base has a minimal role in the subsequent steps. A proton is transferred from –NHTs to the enolate/carbanion leading to **B**. HRMS data analysis of the crude reaction mixture showed the presence of a protonated form of intermediate **A** (or **B**). Finally, an intramolecular nucleophilic substitution by an amine led to the formation of *trans*-DHIs **3** with the removal of dimethyl sulfide.

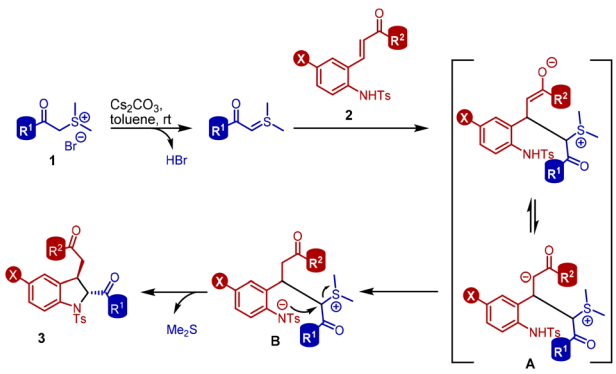
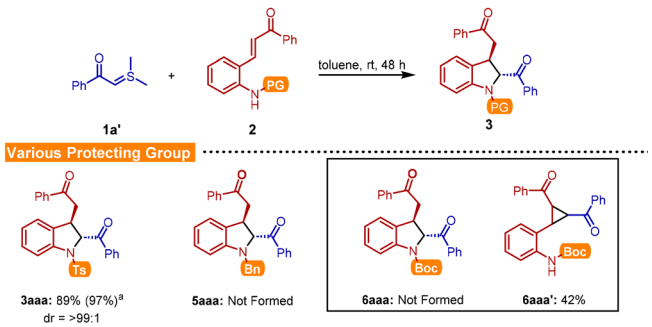


Fig. 2 Plausible mechanism of the [4 + 1] annulation approach.

Table 6 Study of the protecting amino group of **2**

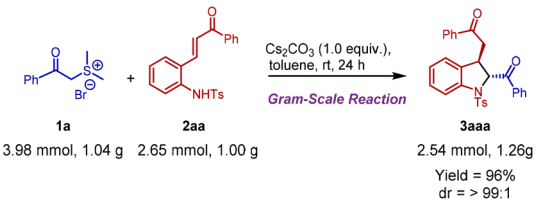


Reaction conditions: **1** (0.3 mmol), **2** (0.2 mmol), and toluene (2 mL), unless specified. [a]The reaction was conducted with 10 mol% of Cs_2CO_3 and the reaction was completed in 24 h.

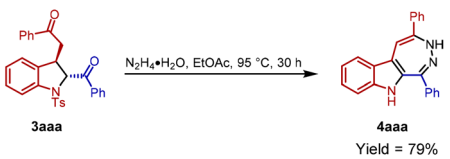
To demonstrate the practicality and scalability of the developed methodology, the [4 + 1] annulation reaction was carried out at the gram-scale, resulting in the formation of product **3aaa** in excellent yield and dr (Scheme 2).

Furthermore, the [4 + 1] annulation reaction was also evaluated using the preformed sulfonium ylide **1a′**. Although, the reaction took a longer time to achieve completion in the absence of any base, the desired DHI **3aaa** was formed in a comparable yield (Table 6). With a catalytic amount of Cs_2CO_3 (10 mol%), the reaction was relatively faster. Next, we tested a variety of protecting groups including Bn and Boc on the nitrogen of *ortho*-aminochalcone **2**. However, the corresponding DHIs did not form with the Bn- and Boc-groups. Surprisingly, the Boc-group protected amine yielded a three-membered product (**6aaa′**) in a moderate yield.

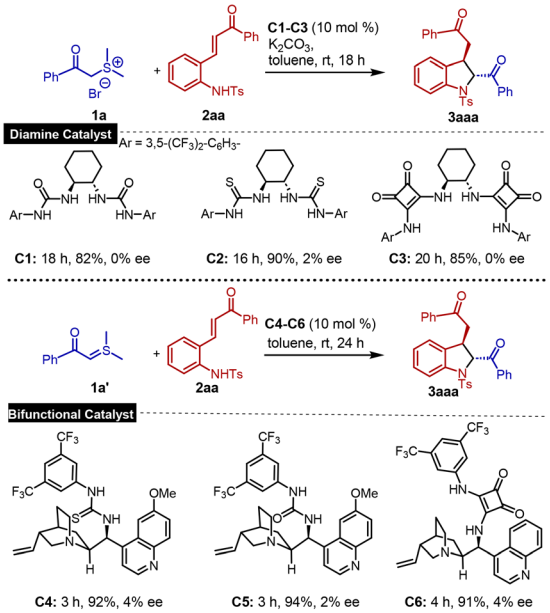
Next, product **3aaa** was transformed into tricyclic diazepino-indole derivative **4aaa**. Interestingly, during this transformation, an intriguing observation on the removal of the tosyl group was made (Scheme 3).



Scheme 2 Cascade synthesis at the gram-scale.



Scheme 3 Synthetic transformations.

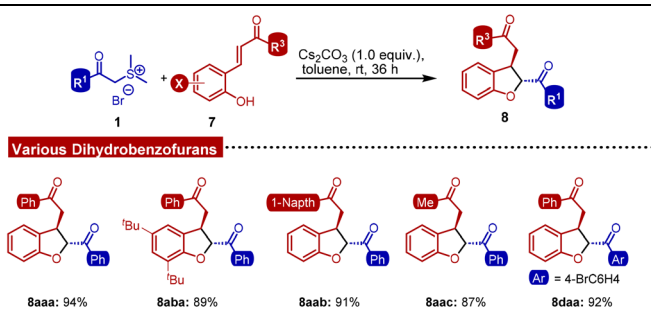


Scheme 4 Asymmetric variant of the cascade [4 + 1] annulation approach.

To access enantioenriched DHIs, reactions were carried out with sulfonium salt **1a** and *ortho*-aminochalcone **2aa** in the presence of chiral cyclohexane-diamine derived H-bond donor catalysts **C1–C3** (Scheme 4). Pleasingly, the cascade reaction proceeded smoothly at room temperature to afford the desired product **3aaa** in a good yield. However, no enantiofacial selectivity was achieved. On the other hand, a similar outcome was observed in the reaction of the preformed sulfur ylide **1a′** and *ortho*-aminochalcone **2aa** in the presence of *Cinchona*-derived bifunctional catalysts **C4–C6** (Scheme 4).

Furthermore, the scope of the reaction was expanded by replacing the aminochalcone with an *ortho*-hydroxychalcone. To our delight, the corresponding DHBs **8** were formed in excellent yields and diastereomeric ratios (Table 7).

Table 7 Synthesis of DHBs



Reaction conditions: **1** (0.3 mmol), **7** (0.2 mmol), Cs_2CO_3 (0.2 mmol), and toluene (2 mL), unless specified. Diastereoisomeric ratios for all entries (>99 : 1) were determined by ^{1}H-NMR analysis.

Conclusions

We have developed a [4 + 1] annulation reaction of *in situ* generated sulfonium ylides with *ortho*-aminochalcones for the synthesis of *trans*-dihydroindoles at room temperature. This cascade approach exhibited tolerance towards a wide variety of substrate groups, demonstrating its ability and versatility to accommodate diverse chemical functionalities. Additionally, successful gram-scale synthesis demonstrates its feasibility and scalability in large-scale manufacturing processes, highlighting its potential for future applications. Importantly, this cascade [4 + 1] annulation reaction was found to be efficient at room temperature under mild reaction conditions. Unlike ammonium ylides which are relatively unstable and cannot be isolated, sulfur ylides can easily be prepared and the same can later be employed in the reactions. All the synthesized dihydroindole derivatives might have significant potential as good candidates for drug discovery and synthetic manipulations. Furthermore, the developed methodology was extended to construct dihydrobenzofurans.

Experimental section

General information

Unless otherwise noted, all reactions were carried out in a closed vial. ^{1}H NMR spectra were recorded on a 500 MHz spectrometer (125 MHz for $^{13}C\{^1H\}$ NMR). The following abbreviations were used to designate chemical shift multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. An oil bath on top of a hot plate was used for heating wherever required. TLC was performed using silica gel GF_{254} precoated on aluminium plates and spots were visualized with UV. Flash column chromatography was performed on silica gel with the use of CombiFlash. IR spectra were recorded on a FT-IR spectrometer and only major peaks were reported in cm^{-1}. High-resolution mass spectra were obtained by the ESI-TOF method (Agilent LC/Q-TOF 6546). Sulfonium salt **1**, *ortho*-aminochalcones **2** and *ortho*-hydroxychalcones **7** were prepared according to the reported methods.[36] All the other reagents were purchased from commercial sources and used as received, unless specified.

General procedure for the synthesis of product 3

The pre-formed sulfonium salt **1** (0.3 mmol) and *ortho*-aminochalcone **2** (0.2 mmol) were added to toluene (2 mL). After stirring the mixture for 5 min, Cs_2CO_3 (65.2 mg, 0.2 mmol) was added and stirring was continued at rt. The progress of the reaction was monitored by TLC. After the completion of the reaction, the crude product **3** was purified by flash column chromatography on a silica support (hexane/ethyl acetate = 5 : 1).

Synthetic procedure for the asymmetric synthesis of product 3aaa. The pre-formed sulfonium salt **1a** (0.3 mmol) and *ortho*-aminochalcone **2aa** (0.2 mmol) were added to toluene (2 mL). The catalyst (**C1–C6**) (0.02 mmol, 10 mol%) was then added. After stirring the mixture for 5 min, K_2CO_3 (0.2 mmol) was added and stirring was continued at rt. The progress of the reaction was monitored by TLC. After the completion of the reaction, the crude product **3aaa** was purified using flash chromatography with hexane/ethyl acetate (5 : 1) as eluents and silica gel (100–200 mesh) as the stationary solid phase.

Synthetic procedure for the scale-up synthesis of product 3aaa. The pre-formed sulfonium salt **1a** (1.04 g, 3.98 mmol) and *ortho*-aminochalcone **2aa** (1.0 g, 2.65 mmol) were added to toluene (25 mL). After stirring the mixture for 5 min, Cs_2CO_3 (0.86 g, 2.65 mmol) was added and stirring was continued at rt. The progress of the reaction was monitored by TLC. After the completion of the reaction, the crude product **3aaa** was purified by flash column chromatography on a silica support (hexane/ethyl acetate = 5 : 1).

2-(2-Benzoyl-1-tosylindolin-3-yl)-1-phenylethan-1-one (3aaa). White solid, yield = 97% (96.1 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, J = 7.6 Hz, 2H), 7.64–7.61 (m, 5H), 7.56–7.46 (m, 2H), 7.43–7.40 (m, 2H), 7.37–7.34 (m, 2H), 7.21 (t, J = 7.9 Hz, 1H), 7.11 (d, J = 7.8 Hz, 2H), 7.03 (d, J = 7.3 Hz, 1H), 6.96 (t, J = 7.4 Hz, 1H), 5.32 (d, J = 2.7 Hz, 1H), 3.82 (s, 1H), 2.89 (dd, J = 17.8, 6.0 Hz, 1H), 2.50 (dd, J = 17.8, 7.7 Hz, 1H), 2.27 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.01, 195.58, 144.47, 141.61, 136.24, 135.18, 134.79, 133.74, 133.71, 133.70, 129.98, 129.32, 128.94, 128.81, 128.76, 128.10, 127.50, 125.11, 124.76, 116.13, 69.80, 44.87, 41.09, 21.70; IR (ATR): ν 3187, 3103, 2980, 2888, 1795, 1772, 1738, 1716, 1695, 1683, 1651, 1634, 1557, 1520, 1506, 1474, 1420, 1362, 1275 cm^{-1}; HRMS (ESI^+) calc. for $C_{30}H_{26}NO_4S$ $[M + H]^+$: 496.1577, found: 496.1585.

Enantioenriched **3aaa** was isolated as a white solid. Enantiomeric excess of the product was determined by chiral stationary phase HPLC analysis using a ChiralPak IA column (70 : 30 hexane/i-PrOH at 1 mL min^{-1}, λ = 254 nm); major enantiomer: t_R = 15.522 min, minor enantiomer: t_R = 28.131 min.

2-(2-(4-Fluorobenzoyl)-1-tosylindolin-3-yl)-1-phenylethan-1-one (3baa). White solid, yield = 91% (93.5 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19–8.05 (m, 2H), 7.68 (dd, J = 15.5, 7.7 Hz, 5H), 7.58 (t, J = 7.3 Hz, 1H), 7.44 (t, J = 7.7 Hz, 2H), 7.29 (t, J = 7.6 Hz, 1H), 7.21–7.12 (m, 4H), 7.10 (d, J = 7.2 Hz, 1H), 7.05 (t, J = 7.4 Hz, 1H), 5.30 (d, J = 3.3 Hz, 1H), 3.92–3.79 (m, 1H), 3.01 (dd, J = 18.0, 5.4 Hz, 1H), 2.50 (dd, J = 18.0, 8.5 Hz, 1H), 2.33 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.16, 194.38, 166.23 ($J_{(C-F)}$ = 253.75 Hz), 144.57, 141.55, 136.16, 134.97, 133.80, 133.77, 132.2 ($J_{(C-F)}$ = 10.00 Hz), 131.25 ($J_{(C-F)}$ = 2.50 Hz), 130.01, 129.00, 128.81, 128.11, 127.49, 124.95, 124.90, 116.17 ($J_{(C-F)}$ = 23.75 Hz), 115.90, 69.58, 44.80, 41.10, 21.71; IR (ATR): ν 3168, 3140, 3138, 3006, 2990, 1796, 1771, 1736, 1716, 1699, 1684, 1652, 1595, 1560, 1541, 1516, 1474, 1415, 1275, 1264 cm^{-1}; HRMS (ESI^+) calc. for $C_{30}H_{25}FNO_4S$ $[M + H]^+$: 514.1483, found: 514.1472.

2-(2-(4-Chlorobenzoyl)-1-tosylindolin-3-yl)-1-phenylethan-1-one (3caa). White solid, yield = 94% (99.6 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, J = 8.6 Hz, 2H), 7.74–7.62 (m, 5H), 7.58 (t, J = 7.4 Hz, 1H), 7.49–7.39 (m, 4H), 7.34–7.27 (m, 1H), 7.16 (d, J = 8.1 Hz, 2H), 7.10 (d, J = 7.3 Hz, 1H), 7.08–7.02 (m, 1H), 5.29

(d, J = 3.4 Hz, 1H), 3.92–3.77 (m, 1H), 3.01 (dd, J = 18.0, 5.4 Hz, 1H), 2.49 (dd, J = 18.0, 8.6 Hz, 1H), 2.33 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.12, 194.85, 144.59, 141.50, 140.22, 136.12, 134.89, 133.80, 133.69, 133.25, 130.84, 130.01, 129.13, 129.01, 128.95, 128.80, 128.10, 127.47, 124.93, 116.27, 69.60, 44.77, 41.05, 21.70; IR (ATR): ν 3158, 3122, 3009, 2988, 1790, 1776, 1735, 1718, 1695, 1652, 1636, 1617, 1560, 1474, 1457, 1419, 1362, 1276, 1263 cm^{-1}; HRMS (ESI$^+$) calc. for $C_{30}H_{24}ClNNaO_4S$ [M + Na]$^+$: 552.1007, found: 552.1005.

2-(2-(4-Bromobenzoyl)-1-tosylindolin-3-yl)-1-phenylethan-1-one (3daa). White solid, yield = 95% (109.2 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, J = 8.6 Hz, 2H), 7.75–7.60 (m, 7H), 7.61–7.54 (m, 1H), 7.43 (t, J = 7.8 Hz, 2H), 7.33–7.27 (m, 1H), 7.16 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 7.3 Hz, 1H), 7.05 (td, J = 7.4, 0.8 Hz, 1H), 5.28 (d, J = 3.5 Hz, 1H), 3.90–3.77 (m, 1H), 3.01 (dd, J = 18.0, 5.4 Hz, 1H), 2.48 (dd, J = 18.1, 8.6 Hz, 1H), 2.33 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.11, 195.06, 144.60, 141.47, 136.09, 134.86, 133.80, 133.67, 133.66, 132.10, 130.90, 130.01, 129.02, 129.00, 128.79, 128.09, 127.45, 124.94, 124.93, 116.26, 69.57, 44.75, 41.03, 21.69; IR (ATR): ν 3150, 3101, 3066, 3006, 2990, 2834, 1795, 1772, 1734, 1717, 1699, 1636, 1559, 1542, 1507, 1474, 1276, 1252 cm^{-1}; HRMS (ESI$^+$) calc. for $C_{30}H_{25}BrNO_4S$ [M + H]$^+$: 574.0682, found: 574.0676.

4-(3-(2-Oxo-2-phenylethyl)-1-tosylindoline-2-carbonyl)benzonitrile (3eaa). White solid, yield = 89% (92.7 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (d, J = 8.3 Hz, 2H), 7.79 (d, J = 8.3 Hz, 2H), 7.69 (dd, J = 7.7, 2.3 Hz, 3H), 7.61 (dd, J = 16.6, 7.8 Hz, 3H), 7.45 (t, J = 7.7 Hz, 2H), 7.37–7.28 (m, 1H), 7.18–7.04 (m, 4H), 5.25 (d, J = 3.6 Hz, 1H), 3.87 (dt, J = 8.7, 4.2 Hz, 1H), 3.07 (dd, J = 18.2, 4.8 Hz, 1H), 2.39 (dd, J = 18.2, 9.3 Hz, 1H), 2.32 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.18, 195.35, 144.78, 141.30, 138.51, 135.96, 134.51, 133.94, 133.47, 132.52, 130.09, 129.80, 129.15, 128.85, 128.09, 127.46, 125.18, 124.85, 118.18, 116.67, 116.49, 69.73, 44.64, 40.86, 21.70; IR (ATR): ν 3141, 3115, 3079, 3005, 2990, 1792, 1774, 1734, 1717, 1699, 1635, 1617, 1541, 1505, 1489, 1474, 1419, 1396, 1362, 1274 cm^{-1}; HRMS (ESI$^+$) calc. for $C_{31}H_{25}N_2O_4S$ [M + H]$^+$: 521.1530, found: 521.1534.

2-(2-(4-Nitrobenzoyl)-1-tosylindolin-3-yl)-1-phenylethan-1-one (3faa). White solid, yield = 85% (91.9 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (d, J = 8.7 Hz, 2H), 8.22 (d, J = 8.7 Hz, 2H), 7.77–7.66 (m, 3H), 7.61 (dd, J = 17.7, 7.8 Hz, 3H), 7.44 (t, J = 7.8 Hz, 2H), 7.38–7.28 (m, 1H), 7.21–7.05 (m, 4H), 5.26 (d, J = 3.6 Hz, 1H), 3.95–3.83 (m, 1H), 3.08 (dd, J = 18.3, 4.7 Hz, 1H), 2.38 (dd, J = 18.3, 9.4 Hz, 1H), 2.32 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.19, 195.35, 150.51, 144.83, 141.27, 140.16, 135.93, 134.44, 133.96, 133.44, 130.42, 130.10, 129.19, 128.85, 128.09, 127.46, 125.22, 124.85, 123.85, 116.52, 69.92, 44.65, 40.85, 21.70; IR (ATR): ν 3130, 3115, 3005, 2989, 2879, 1790, 1771, 1750, 1733, 1716, 1634, 1684, 1663, 1617, 1559, 1522, 1489, 1474, 1434, 1397, 1275, 1262 cm^{-1}; HRMS (ESI$^+$) calc. for $C_{30}H_{25}N_2O_6S$ [M + H]$^+$: 541.1428, found: 541.1420.

2-(2-(4-Methylbenzoyl)-1-tosylindolin-3-yl)-1-phenylethan-1-one (3gaa). White solid, yield = 93% (94.8 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, J = 8.0 Hz, 2H), 7.77–7.61 (m, 5H), 7.56 (t, J = 6.8 Hz, 1H), 7.42 (t, J = 7.1 Hz, 2H), 7.33–7.24 (m, 3H), 7.18 (d, J = 7.8 Hz, 2H), 7.08 (d, J = 7.4 Hz, 1H), 7.01 (t, J = 7.4 Hz, 1H), 5.35 (d, J = 3.3 Hz, 1H), 3.87 (s, 1H), 2.95 (dd, J = 17.8, 6.2 Hz, 1H), 2.60 (dd, J = 17.8, 7.6 Hz, 1H), 2.42 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.04, 195.12, 144.67, 144.41, 141.67, 136.29, 135.26, 133.83, 133.67, 132.18, 129.96, 129.56, 129.47, 128.90, 128.76, 128.12, 127.51, 125.10, 124.69, 116.07, 69.72, 44.89, 41.17, 21.90, 21.71; IR (ATR): ν 3123, 3099, 3006, 2989, 1792, 1771, 1735, 1718, 1698, 1685, 1640, 1620, 1542, 1517, 1474, 1419, 1263 cm^{-1}; HRMS (ESI$^+$) calc. for $C_{31}H_{27}NNaO_4S$ [M + Na]$^+$: 532.1553, found: 532.1550.

2-(2-(2-Methoxybenzoyl)-1-tosylindolin-3-yl)-1-phenylethan-1-one (3haa). White solid, yield = 90% (94.6 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76–7.67 (m, 3H), 7.67–7.60 (m, 3H), 7.55 (t, J = 7.4 Hz, 1H), 7.53–7.47 (m, 1H), 7.41 (t, J = 7.7 Hz, 2H), 7.26–7.20 (m, 3H), 7.10–7.01 (m, 2H), 6.98–6.91 (m, 2H), 5.50 (d, J = 2.8 Hz, 1H), 4.01–3.93 (m, 1H), 3.70 (s, 3H), 2.74 (qd, J = 17.4, 6.8 Hz, 2H), 2.40 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.05, 196.81, 158.40, 144.22, 141.87, 136.53, 135.84, 134.19, 134.17, 133.51, 131.77, 129.85, 128.75, 128.69, 128.04, 127.55, 125.80, 125.43, 124.48, 121.33, 115.97, 111.49, 73.69, 55.59, 45.74, 40.38, 21.76; IR (ATR): ν 3110, 3079, 3055, 3006, 2990, 2888, 1792, 1774, 1750, 1717, 1699, 1679, 1653, 1617, 1521, 1489, 1473, 1419, 1263 cm^{-1}; HRMS (ESI$^+$) calc. for $C_{31}H_{28}NO_5S$ [M + H]$^+$: 526.1683, found: 526.1691.

2-(2-(3-Methoxybenzoyl)-1-tosylindolin-3-yl)-1-phenylethan-1-one (3iaa). White solid, yield = 94% (98.8 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (dd, J = 13.1, 4.7 Hz, 5H), 7.62 (d, J = 7.7 Hz, 1H), 7.60–7.53 (m, 2H), 7.40 (dt, J = 19.4, 7.9 Hz, 3H), 7.30–7.26 (m, 1H), 7.19 (d, J = 8.0 Hz, 2H), 7.14 (ddd, J = 8.2, 2.6, 0.6 Hz, 1H), 7.09 (d, J = 7.5 Hz, 1H), 7.02 (td, J = 7.5, 0.8 Hz, 1H), 5.35 (d, J = 3.3 Hz, 1H), 3.89 (td, J = 7.0, 3.3 Hz, 1H), 3.83 (s, 3H), 2.95 (dd, J = 17.8, 6.3 Hz, 1H), 2.60 (dd, J = 17.8, 7.7 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.97, 195.33, 159.94, 144.46, 141.62, 136.25, 136.03, 135.24, 133.71, 133.69, 129.98, 129.77, 128.95, 128.76, 128.10, 127.49, 125.15, 124.74, 121.84, 120.59, 116.09, 113.34, 70.07, 55.52, 44.89, 41.16, 21.70; IR (ATR): ν 3115, 3098, 3006, 2989, 1792, 1770, 1734, 1717, 1699, 1684, 1636, 1559, 1541, 1507, 1489, 1457, 1369, 1275 cm^{-1}; HRMS (ESI$^+$) calc. for $C_{31}H_{28}NO_5S$ [M + H]$^+$: 526.1683, found: 526.1684.

2-(2-(4-Methoxybenzoyl)-1-tosylindolin-3-yl)-1-phenylethan-1-one (3jaa). White solid, yield = 96% (100.9 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, J = 8.8 Hz, 2H), 7.69 (dt, J = 13.1, 5.9 Hz, 5H), 7.57 (t, J = 7.4 Hz, 1H), 7.43 (t, J = 7.7 Hz, 2H), 7.28 (d, J = 7.6 Hz, 1H), 7.18 (d, J = 8.1 Hz, 2H), 7.09 (d, J = 7.4 Hz, 1H), 7.02 (t, J = 7.5 Hz, 1H), 6.97 (d, J = 8.9 Hz, 2H), 5.34 (d, J = 3.3 Hz, 1H), 3.88 (s, 4H), 2.98 (dd, J = 17.9, 6.0 Hz, 1H), 2.58 (dd, J = 17.9, 7.9 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.15, 194.02, 164.12, 144.39, 141.72, 136.30, 135.24, 133.97, 133.68, 131.79, 129.95, 128.87, 128.77, 128.13, 127.59, 127.52, 125.04, 124.69, 116.08, 114.11, 69.47, 55.64, 44.88, 41.29, 21.71; IR (ATR): ν 3135, 3109, 3081, 3066, 3006, 2990, 1792, 1772, 1734, 1699, 1684, 1636, 1559, 1541, 1507, 1473, 1457, 1276, 1261 cm^{-1}; HRMS (ESI$^+$) calc. for $C_{31}H_{28}NO_5S$ [M + H]$^+$: 526.1683, found: 526.1676.

2-(2-(2,4-Dichlorobenzoyl)-1-tosylindolin-3-yl)-1-phenylethan-1-one (3kaa). White solid, yield = 84% (94.8 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, J = 8.1 Hz, 1H), 7.63–7.54 (m, 5H), 7.49 (d, J = 8.3 Hz, 1H), 7.46–7.38 (m, 3H), 7.33 (dd, J = 8.3, 1.9 Hz, 1H), 7.31–7.26 (m, 1H), 7.13 (d, J = 7.4 Hz, 1H), 7.12–7.04 (m, 3H), 5.22 (d, J = 2.2 Hz, 1H), 4.04–3.94 (m, 1H), 2.81 (dd, J = 17.9, 5.3 Hz, 1H), 2.29 (s, 3H), 2.06 (dd, J = 17.9, 9.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.24, 196.79, 144.65, 140.97, 137.35, 136.01, 135.81, 134.83, 134.13, 133.68, 132.44, 130.33, 130.20, 130.03, 129.02, 128.73, 127.99, 127.40, 127.13, 125.43, 125.05, 117.24, 72.02, 44.82, 39.33, 21.69; IR (ATR): ν 3121, 3103, 3081, 3006, 2991, 1790, 1772, 1749, 1734, 1717, 1670, 1653, 1617, 1565, 1542, 1490, 1457, 1420, 1400, 1261 cm^{-1}; HRMS (ESI$^+$) calc. for $C_{30}H_{24}Cl_2NO_4S$ [M + H]$^+$: 564.0798, found: 564.0793.

2-(2-(3,4-Dichlorobenzoyl)-1-tosylindolin-3-yl)-1-phenylethan-1-one (3laa). White solid, yield = 91% (102.7 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, J = 2.0 Hz, 1H), 7.92 (dd, J = 8.4, 2.0 Hz, 1H), 7.70 (dd, J = 9.7, 8.3 Hz, 3H), 7.64 (d, J = 8.3 Hz, 2H), 7.59 (dd, J = 14.3, 7.9 Hz, 2H), 7.44 (t, J = 7.8 Hz, 2H), 7.34–7.27 (m, 1H), 7.15 (d, J = 8.1 Hz, 2H), 7.08 (dt, J = 14.6, 7.0 Hz, 2H), 5.23 (d, J = 3.5 Hz, 1H), 3.85 (dt, J = 8.7, 4.3 Hz, 1H), 3.05 (dd, J = 18.1, 5.0 Hz, 1H), 2.45 (dd, J = 18.1, 9.2 Hz, 1H), 2.33 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.19, 194.13, 144.70, 141.41, 138.29, 136.05, 134.76, 134.63, 133.89, 133.52, 133.50, 131.43, 130.83, 130.05, 129.10, 128.84, 128.48, 128.13, 127.48, 125.04, 124.87, 116.36, 69.58, 44.70, 41.03, 21.71; IR (ATR): ν 3102, 3080, 3006, 2990, 2926, 1790, 1775, 1734, 1717, 1698, 1684, 1641, 1617, 1560, 1510, 1473, 1419, 1260 cm^{-1}; HRMS (ESI$^+$) calc. for $C_{30}H_{24}Cl_2NO_4S$ [M + H]$^+$: 564.0798, found: 564.0795.

2-(2-(2-Naphthoyl)-1-tosylindolin-3-yl)-1-phenylethan-1-one (3maa). White solid, yield = 94% (102.6 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.66 (s, 1H), 8.03 (dd, J = 8.6, 1.7 Hz, 1H), 7.97 (d, J = 8.1 Hz, 1H), 7.89 (dd, J = 11.0, 8.6 Hz, 2H), 7.77–7.65 (m, 5H), 7.65–7.59 (m, 1H), 7.57–7.50 (m, 2H), 7.41 (t, J = 7.8 Hz, 2H), 7.30 (t, J = 7.8 Hz, 1H), 7.18 (d, J = 8.0 Hz, 2H), 7.11 (d, J = 7.5 Hz, 1H), 7.04 (td, J = 7.5, 0.9 Hz, 1H), 5.56 (d, J = 3.2 Hz, 1H), 3.98–3.91 (m, 1H), 3.04 (dd, J = 17.8, 5.8 Hz, 1H), 2.68 (dd, J = 17.8, 8.2 Hz, 1H), 2.33 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.11, 195.52, 144.45, 141.71, 136.24, 135.96, 135.37, 133.78, 133.70, 132.61, 132.05, 131.44, 130.09, 129.97, 128.97, 128.85, 128.77, 128.66, 128.13, 127.89, 127.50, 126.84, 125.06, 124.74, 124.71, 116.04, 69.98, 44.93, 41.39, 21.69; IR (ATR): ν 3135, 3102, 3067, 3006, 2990, 1795, 1772, 1749, 1734, 1717, 1698, 1684, 1636, 1559, 1541, 1457, 1257 cm^{-1}; HRMS (ESI$^+$) calc. for $C_{34}H_{28}NO_4S$ [M + H]$^+$: 546.1734, found: 546.1730.

2-(2-([1,1′-Biphenyl]-4-carbonyl)-1-tosylindolin-3-yl)-1-phenylethan-1-one (3naa). White solid, yield = 93% (106.3 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, J = 8.3 Hz, 2H), 7.78–7.67 (m, 7H), 7.67–7.61 (m, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.48 (t, J = 7.5 Hz, 2H), 7.42 (dd, J = 15.9, 7.9 Hz, 3H), 7.30 (t, J = 7.8 Hz, 1H), 7.19 (d, J = 8.1 Hz, 2H), 7.11 (d, J = 7.4 Hz, 1H), 7.04 (t, J = 7.2 Hz, 1H), 5.40 (d, J = 3.4 Hz, 1H), 3.97–3.89 (m, 1H), 3.01 (dd, J = 17.9, 6.0 Hz, 1H), 2.62 (dd, J = 17.9, 7.9 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.08, 195.21, 146.34, 144.48, 141.64, 140.04, 136.23, 135.13, 133.79, 133.71, 133.43, 129.98, 129.96, 129.07, 128.94, 128.77, 128.38, 128.11, 127.51, 127.47, 127.45, 125.08, 124.77, 116.12, 69.78, 44.87, 41.19, 21.70; IR (ATR): ν 3152, 3113, 3006, 2989, 1792, 1773, 1734, 1717, 1699, 1653, 1603, 1559, 1541, 1507, 1489, 1419, 1397, 1262 cm^{-1}; HRMS (ESI$^+$) calc. for $C_{36}H_{30}NO_4S$ [M + H]$^+$: 572.1890, found: 572.1877.

2-(2-(Furan-2-carbonyl)-1-tosylindolin-3-yl)-1-phenylethan-1-one (3oaa). White solid, yield = 88% (85.5 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76–7.63 (m, 5H), 7.60–7.56 (m, 2H), 7.48 (dd, J = 3.6, 0.5 Hz, 1H), 7.43 (t, J = 7.8 Hz, 2H), 7.31–7.26 (m, 1H), 7.21 (d, J = 8.0 Hz, 2H), 7.09 (d, J = 7.5 Hz, 1H), 7.02 (td, J = 7.5, 0.9 Hz, 1H), 6.58 (dd, J = 3.6, 1.7 Hz, 1H), 5.09 (d, J = 3.7 Hz, 1H), 3.95 (td, J = 6.9, 3.7 Hz, 1H), 2.89 (dd, J = 17.7, 6.7 Hz, 1H), 2.67 (dd, J = 17.8, 7.2 Hz, 1H), 2.36 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.89, 184.10, 150.54, 147.45, 144.56, 141.59, 136.34, 134.88, 133.70, 133.69, 129.99, 128.94, 128.79, 128.10, 127.63, 125.18, 124.86, 120.20, 116.19, 112.87, 70.41, 45.08, 41.18, 21.74; IR (ATR): ν 3019, 3006, 2990, 2925, 2856, 1793, 1770, 1749, 1734, 1684, 1653, 1559, 1507, 1458, 1276, 1259 cm^{-1}; HRMS (ESI$^+$) calc. for $C_{28}H_{24}NO_5S$ [M + H]$^+$: 486.1370, found: 486.1384.

1-Phenyl-2-(2-(thiophene-2-carbonyl)-1-tosylindolin-3-yl)ethan-1-one (3paa). White solid, yield = 87% (87.3 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (dd, J = 3.8, 1.0 Hz, 1H), 7.74–7.68 (m, 6H), 7.56 (dd, J = 10.5, 4.3 Hz, 1H), 7.42 (t, J = 7.8 Hz, 2H), 7.29 (t, J = 7.7 Hz, 1H), 7.25–7.13 (m, 3H), 7.09 (d, J = 7.4 Hz, 1H), 7.04 (dd, J = 10.8, 4.1 Hz, 1H), 5.06 (d, J = 3.8 Hz, 1H), 3.95 (dd, J = 10.4, 6.8 Hz, 1H), 2.94 (dd, J = 18.0, 6.3 Hz, 1H), 2.57 (dd, J = 18.0, 7.6 Hz, 1H), 2.33 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.94, 188.84, 144.65, 141.48, 140.74, 136.17, 135.34, 134.45, 134.33, 133.79, 133.66, 129.97, 128.88, 128.73, 128.47, 128.03, 127.52, 125.05, 124.97, 116.20, 71.19, 44.71, 41.50, 21.66; IR (ATR): ν 3130, 3095, 3005, 2988, 1791, 1772, 1735, 1716, 1699, 1683, 1652, 1616, 1560, 1541, 1505, 1489, 1456, 1360, 1263 cm^{-1}; HRMS (ESI$^+$) calc. for $C_{28}H_{24}NO_4S_2$ [M + H]$^+$: 502.1141, found: 502.1138.

2-(2-((1*S*,3*S*)-Adamantane-1-carbonyl)-1-tosylindolin-3-yl)-1-phenylethan-1-one (3qaa). White solid, yield = 85% (94.1 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, J = 8.2 Hz, 2H), 7.63 (dd, J = 12.7, 4.7 Hz, 3H), 7.57 (t, J = 7.4 Hz, 1H), 7.42 (t, J = 7.8 Hz, 2H), 7.26–7.19 (m, 3H), 7.05 (d, J = 7.4 Hz, 1H), 6.94 (t, J = 7.5 Hz, 1H), 5.00 (d, J = 1.8 Hz, 1H), 3.62 (t, J = 6.3 Hz, 1H), 2.60 (dd, J = 17.5, 8.1 Hz, 1H), 2.54–2.42 (m, 1H), 2.36 (d, J = 16.2 Hz, 3H), 2.04 (dd, J = 24.6, 7.3 Hz, 6H), 1.93 (d, J = 12.2 Hz, 3H), 1.80–1.72 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.55, 196.84, 144.31, 141.86, 136.34, 135.76, 134.26, 133.68, 129.96, 128.81, 128.74, 128.07, 127.31, 125.45, 124.66, 116.23, 67.50, 46.31, 45.33, 40.64, 38.27, 36.51, 27.99, 21.71; IR (ATR): ν 3069, 3005, 2990, 2910, 2851, 1792, 1770, 1724, 1717, 1700, 1683, 1653, 1559, 1541, 1507, 1455, 1277 cm^{-1}; HRMS (ESI$^+$) calc. for $C_{34}H_{36}NO_4S$ [M + H]$^+$: 554.2360, found: 554.2370.

2,2-Dimethyl-1-(3-(2-oxo-2-phenylethyl)-1-tosylindolin-2-yl) propan-1-one (3raa). White solid, yield = 90% (85.6 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (dd, J = 12.0, 8.2 Hz, 3H),

7.63–7.59 (m, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.42 (t, J = 7.8 Hz, 2H), 7.22 (dd, J = 14.0, 8.1 Hz, 3H), 7.05 (d, J = 7.5 Hz, 1H), 6.97 (t, J = 7.5 Hz, 1H), 4.97 (d, J = 1.8 Hz, 1H), 3.64 (t, J = 6.4 Hz, 1H), 2.60 (dd, J = 17.7, 7.6 Hz, 1H), 2.45–2.28 (m, 4H), 1.31 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.87, 196.83, 144.37, 141.91, 136.33, 135.65, 134.51, 133.70, 129.98, 128.87, 128.77, 128.06, 127.36, 125.31, 124.86, 116.59, 68.03, 45.40, 44.14, 41.04, 26.93, 21.73; IR (ATR): ν 3066, 3005, 2965, 2921, 2851, 1772, 1716, 1681, 1653, 1634, 1597, 1579, 1559, 1540, 1530, 1507, 1477, 1459, 1398, 1355, 1275, 1257 cm^{-1}; HRMS (ESI^+) calc. for $C_{28}H_{30}NO_4S$ $[M + H]^+$: 476.1890, found: 476.1875.

2-(2-Acetyl-1-tosylindolin-3-yl)-1-phenylethan-1-one (3saa). White solid, yield = 89% (77.2 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05–7.95 (m, 2H), 7.72 (d, J = 8.3 Hz, 2H), 7.60 (t, J = 8.5 Hz, 2H), 7.48 (t, J = 7.7 Hz, 2H), 7.26 (dd, J = 12.9, 5.2 Hz, 3H), 7.07–6.97 (m, 2H), 5.23 (d, J = 4.0 Hz, 1H), 3.78–3.53 (m, 1H), 2.48 (dd, J = 17.9, 6.5 Hz, 1H), 2.40 (s, 3H), 2.28 (dd, J = 17.9, 7.4 Hz, 1H), 1.97 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.70, 195.55, 144.56, 141.51, 135.10, 134.68, 133.73, 133.06, 129.90, 129.23, 128.93, 128.82, 127.61, 124.95, 124.54, 115.55, 70.12, 49.25, 40.77, 30.18, 21.68; IR (ATR): ν 3065, 3005, 2991, 1790, 1764, 1733, 1685, 1617, 1594, 1540, 1474, 1420, 1362, 1262 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{25}H_{24}NO_4S$: 434.1421; found: 434.1430.

Ethyl 3-(2-oxo-2-phenylethyl)-1-tosylindoline-2-carboxylate (3taa). White solid, yield = 87% (80.7 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69–7.65 (m, 5H), 7.57 (t, J = 7.4 Hz, 1H), 7.43 (t, J = 7.8 Hz, 2H), 7.25 (dd, J = 9.6, 5.4 Hz, 1H), 7.16 (d, J = 8.1 Hz, 2H), 7.10 (d, J = 7.5 Hz, 1H), 7.01 (t, J = 7.5 Hz, 1H), 4.48 (d, J = 3.4 Hz, 1H), 4.27–4.23 (m, 2H), 4.03–3.88 (m, 1H), 2.83 (dd, J = 17.8, 6.2 Hz, 1H), 2.41 (dd, J = 17.8, 8.0 Hz, 1H), 2.33 (s, 3H), 1.29 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.71, 170.33, 144.46, 141.19, 136.28, 135.00, 133.62, 133.57, 129.93, 128.83, 128.74, 128.05, 127.46, 124.94, 124.78, 116.30, 77.41, 77.16, 76.91, 67.99, 62.02, 44.96, 41.03, 21.67, 14.19; IR (ATR): ν 3168, 3112, 3068, 3010, 2995, 1842, 1801, 1778, 1760, 1735, 1716, 1684, 1541, 1475, 1332 cm^{-1}; HRMS (ESI^+) calc. for $C_{26}H_{26}NO_5S^+$ $[M + H]^+$: 464.1526, found: 464.1530.

2-(2-Benzoyl-5-fluoro-1-tosylindolin-3-yl)-1-phenylethan-1-one (3aba). White solid, yield = 90% (92.4 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (dd, J = 8.2, 0.9 Hz, 2H), 7.76–7.54 (m, 7H), 7.47 (dt, J = 32.5, 7.8 Hz, 4H), 7.19 (d, J = 8.1 Hz, 2H), 6.98 (td, J = 8.8, 2.6 Hz, 1H), 6.83 (dd, J = 8.1, 2.5 Hz, 1H), 5.39 (d, J = 3.0 Hz, 1H), 3.94–3.75 (m, 1H), 2.88 (dd, J = 18.0, 6.3 Hz, 1H), 2.48 (dd, J = 18.0, 7.8 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.67, 195.38, 160.37 ($J_{(C–F)}$ = 242.50 Hz), 144.68, 137.66, 136.22 ($J_{(C–F)}$ = 8.75 Hz), 136.05, 134.79 ($J_{(C–F)}$ = 26.25 Hz), 133.88, 133.84, 130.09, 129.33, 128.88, 128.81, 128.09, 127.52, 117.62 ($J_{(C–F)}$ = 7.5 Hz), 115.60 ($J_{(C–F)}$ = 22.50 Hz), 112.69, 112.49, 69.66, 44.53, 40.89, 21.73; IR (ATR): ν 3136, 3006, 2990, 1792, 1770, 1717, 1698, 1652, 1597, 1558, 1540, 1517, 1474, 1415, 1263 cm^{-1}; HRMS (ESI^+) calc. for $C_{30}H_{25}FNO_4S$ $[M + H]^+$: 514.1483, found: 514.1482.

2-(2-Benzoyl-5-chloro-1-tosylindolin-3-yl)-1-phenylethan-1-one (3aca). White solid, yield = 90% (95.4 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07–8.00 (m, 2H), 7.73–7.64 (m, 4H), 7.62–7.59 (m, 3H), 7.50 (t, J = 7.8 Hz, 2H), 7.44 (t, J = 7.8 Hz, 2H), 7.26–7.23 (m, 1H), 7.19 (d, J = 8.1 Hz, 2H), 7.09 (d, J = 1.7 Hz, 1H), 5.40 (d, J = 3.1 Hz, 1H), 3.88–3.72 (m, 1H), 2.92 (dd, J = 18.0, 6.1 Hz, 1H), 2.52 (dd, J = 18.0, 7.9 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.61, 195.27, 144.76, 140.42, 136.02, 135.89, 134.95, 134.62, 133.91, 133.86, 130.12, 130.04, 129.33, 129.01, 128.89, 128.82, 128.10, 127.46, 125.44, 117.24, 69.60, 44.60, 40.87, 21.73; IR (ATR): ν 3120, 3005, 2989, 1792, 1771, 1733, 1716, 1699, 1636, 1617, 1559, 1475, 1457, 1418, 1362, 1264 cm^{-1}; HRMS (ESI^+) calc. for $C_{30}H_{25}ClNO_4S$ $[M + H]^+$: 530.1187, found: 530.1163.

2-(2-Benzoyl-5-bromo-1-tosylindolin-3-yl)-1-phenylethan-1-one (3ada). White solid, yield = 94% (108.0 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07–7.99 (m, 2H), 7.71–7.65 (m, 4H), 7.65–7.54 (m, 3H), 7.50 (t, J = 7.8 Hz, 2H), 7.46–7.37 (m, 3H), 7.23 (d, J = 1.5 Hz, 1H), 7.19 (d, J = 8.1 Hz, 2H), 5.40 (d, J = 3.1 Hz, 1H), 3.89–3.78 (m, 1H), 2.93 (dd, J = 18.0, 6.0 Hz, 1H), 2.52 (dd, J = 18.0, 8.0 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.60, 195.23, 144.77, 140.94, 136.23, 135.98, 134.91, 134.58, 133.90, 133.85, 131.88, 130.12, 129.31, 128.87, 128.81, 128.29, 128.08, 127.41, 117.62, 117.50, 69.50, 44.62, 40.82, 21.71; IR (ATR): ν 3101, 3005, 2990, 2835, 1795, 1771, 1734, 1717, 1698, 1636, 1559, 1542, 1507, 1473, 1276, 1234 cm^{-1}; HRMS (ESI^+) calc. for $C_{30}H_{25}BrNO_4S$ $[M + H]^+$: 574.0682, found: 574.0688.

2-(2-Benzoyl-1-tosylindolin-3-yl)-1-(4-fluorophenyl)ethan-1-one (3aab). White solid, yield = 95% (97.6 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, J = 8.1 Hz, 2H), 7.79–7.68 (m, 4H), 7.65 (d, J = 8.1 Hz, 1H), 7.63–7.57 (m, 1H), 7.55–7.45 (m, 2H), 7.34–7.27 (m, 1H), 7.20 (d, J = 8.0 Hz, 2H), 7.09 (t, J = 7.7 Hz, 3H), 7.02 (t, J = 7.5 Hz, 1H), 5.36 (d, J = 3.5 Hz, 1H), 3.89 (dd, J = 9.4, 6.9 Hz, 1H), 2.97 (dd, J = 17.7, 6.1 Hz, 1H), 2.62 (dd, J = 17.7, 7.7 Hz, 1H), 2.36 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.57, 195.43, 166.09 ($J_{(C–F)}$ = 255.00 Hz), 144.45, 141.62, 135.24, 134.78, 133.75, 133.52, 132.53 ($J_{(C–F)}$ = 3.75 Hz), 130.82 ($J_{(C–F)}$ = 8.75 Hz), 129.96, 129.32, 129.02, 128.83, 127.59, 124.01 ($J_{(C–F)}$ = 43.75 Hz), 116.03, 116.01, 115.83, 69.91, 44.71, 41.10, 21.73; IR (ATR): ν 3005, 2990, 2980, 1790, 1735, 1716, 1684, 1652, 1636, 1559, 1542, 1457, 1276, 1263 cm^{-1}; HRMS (ESI^+) calc. for $C_{30}H_{25}FNO_4S$ $[M + H]^+$: 514.1483, found: 514.1484.

2-(2-Benzoyl-1-tosylindolin-3-yl)-1-(4-chlorophenyl)ethan-1-one (3aac). White solid, yield = 93% (98.6 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, J = 7.3 Hz, 2H), 7.70 (d, J = 8.2 Hz, 2H), 7.68–7.56 (m, 4H), 7.49 (t, J = 7.8 Hz, 2H), 7.39 (d, J = 8.5 Hz, 2H), 7.28 (t, J = 7.8 Hz, 1H), 7.19 (d, J = 8.1 Hz, 2H), 7.08 (d, J = 7.4 Hz, 1H), 7.02 (t, J = 7.4 Hz, 1H), 5.35 (d, J = 3.5 Hz, 1H), 3.88 (td, J = 7.2, 3.6 Hz, 1H), 2.96 (dd, J = 17.8, 6.1 Hz, 1H), 2.61 (dd, J = 17.8, 7.8 Hz, 1H), 2.36 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.85, 195.54, 144.47, 141.62, 140.25, 135.22, 134.77, 134.56, 133.76, 133.46, 129.97, 129.53, 129.32, 129.10, 129.04, 128.84, 127.57, 125.06, 124.75, 116.06, 69.87, 44.75, 41.05, 21.74; IR (ATR): ν 3064, 3006, 2990, 2956, 2923, 2852, 1791, 1778, 1751, 1735, 1698, 1685, 1652, 1636, 1558, 1541, 1458, 1276, 1255 cm^{-1}; HRMS (ESI^+) calc. for $C_{30}H_{25}ClNO_4S$ $[M + H]^+$: 530.1187, found: 530.1160.

2-(2-Benzoyl-1-tosylindolin-3-yl)-1-(4-bromophenyl)ethan-1-one (3aad). White solid, yield = 97% (111.5 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07–8.00 (m, 2H), 7.70 (d, J = 8.3 Hz, 2H), 7.66 (d, J = 8.1 Hz, 1H), 7.63–7.58 (m, 1H), 7.58–7.53 (m, 4H), 7.48 (dd, J = 10.7, 4.8 Hz, 2H), 7.33–7.26 (m, 1H), 7.19 (d, J = 8.0 Hz, 2H), 7.07 (d, J = 7.4 Hz, 1H), 7.02 (td, J = 7.5, 0.9 Hz, 1H), 5.35 (d, J = 3.5 Hz, 1H), 3.88 (td, J = 7.3, 3.5 Hz, 1H), 2.96 (dd, J = 17.8, 6.1 Hz, 1H), 2.60 (dd, J = 17.9, 7.8 Hz, 1H), 2.36 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.06, 195.54, 144.47, 141.60, 135.20, 134.95, 134.76, 133.76, 133.44, 132.09, 129.96, 129.61, 129.31, 129.04, 128.98, 128.83, 127.56, 125.05, 124.75, 116.05, 69.84, 44.72, 41.03, 21.73; IR (ATR): ν 3105, 3057, 3004, 2988, 1789, 1776, 1750, 1730, 1717, 1636, 1607, 1522, 1489, 1437, 1361, 1220 cm^{-1}; HRMS (ESI$^+$) calc. for $C_{30}H_{25}BrNO_4S$ [M + H]$^+$: 574.0682, found: 574.0686.

4-(2-(2-Benzoyl-1-tosylindolin-3-yl)acetyl)benzonitrile (3aae). White solid, yield = 90% (93.7 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, J = 7.6 Hz, 2H), 7.79 (d, J = 8.2 Hz, 2H), 7.75–7.66 (m, 4H), 7.66–7.57 (m, 2H), 7.48 (t, J = 7.6 Hz, 2H), 7.33–7.26 (m, 1H), 7.20 (d, J = 7.9 Hz, 2H), 7.07 (d, J = 7.5 Hz, 1H), 7.02 (t, J = 7.4 Hz, 1H), 5.35 (d, J = 1.5 Hz, 1H), 3.90 (dd, J = 9.9, 6.7 Hz, 1H), 3.04 (dd, J = 18.0, 6.1 Hz, 1H), 2.73 (dd, J = 18.0, 7.5 Hz, 1H), 2.36 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.84, 195.44, 144.51, 141.60, 139.01, 135.19, 134.71, 133.83, 133.05, 132.61, 129.95, 129.27, 129.17, 128.86, 128.54, 127.63, 125.03, 124.74, 117.79, 116.99, 115.96, 69.93, 44.94, 40.89, 21.73; IR (ATR): ν 3110, 3066, 3004, 2990, 2891, 1792, 1771, 1750, 1718, 1683, 1634, 1617, 1571, 1507, 1472, 1430, 1390, 1278 cm^{-1}; HRMS (ESI$^+$) calc. for $C_{31}H_{25}N_2O_4S$ [M + H]$^+$: 521.1530, found: 521.1535.

2-(2-Benzoyl-1-tosylindolin-3-yl)-1-(*p*-tolyl)ethan-1-one (3aaf). White solid, yield = 92% (93.8 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17–7.94 (m, 2H), 7.69 (dd, J = 12.8, 8.2 Hz, 3H), 7.59 (t, J = 8.8 Hz, 3H), 7.48 (t, J = 7.7 Hz, 2H), 7.28 (d, J = 7.5 Hz, 1H), 7.20 (dd, J = 10.0, 8.5 Hz, 4H), 7.09 (d, J = 7.4 Hz, 1H), 7.02 (dd, J = 7.5, 6.9 Hz, 1H), 5.37 (d, J = 3.4 Hz, 1H), 3.88 (td, J = 7.4, 3.4 Hz, 1H), 2.94 (dd, J = 17.7, 6.2 Hz, 1H), 2.57 (dd, J = 17.7, 7.8 Hz, 1H), 2.41 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.63, 195.61, 144.62, 144.43, 141.61, 135.21, 134.80, 133.85, 133.81, 133.69, 129.97, 129.43, 129.33, 128.90, 128.80, 128.25, 127.51, 125.12, 124.71, 116.06, 69.87, 44.76, 41.17, 21.82, 21.72; IR (ATR): ν 3115, 3006, 2988, 1793, 1734, 1716, 1699, 1653, 1636, 1606, 1522, 1507, 1489, 1474, 1438, 1397, 1274 cm^{-1}; HRMS (ESI$^+$) calc. for $C_{31}H_{28}NO_4S$ [M + H]$^+$: 510.1734, found: 510.1709.

2-(2-Benzoyl-1-tosylindolin-3-yl)-1-(2-methoxyphenyl)ethan-1-one (3aag). White solid, yield = 90% (94.6 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08–7.97 (m, 2H), 7.73 (d, J = 8.3 Hz, 2H), 7.61–7.57 (m, 3H), 7.52–7.42 (m, 3H), 7.27–7.22 (m, 1H), 7.17 (d, J = 8.1 Hz, 2H), 7.08 (d, J = 7.4 Hz, 1H), 7.01–6.97 (m, 2H), 6.91 (d, J = 8.3 Hz, 1H), 5.41 (d, J = 4.0 Hz, 1H), 3.97–3.82 (m, 1H), 3.77 (s, 3H), 3.17 (dd, J = 17.4, 5.9 Hz, 1H), 2.81 (dd, J = 17.4, 8.0 Hz, 1H), 2.32 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.07, 196.04, 158.75, 144.28, 141.64, 135.22, 134.89, 134.27, 133.59, 133.57, 130.61, 129.80, 129.29, 128.75, 128.68, 127.57, 127.37, 125.01, 124.28, 120.91, 115.18, 111.65, 70.10, 55.54, 49.92, 41.66, 21.67; IR (ATR): ν 3080, 3064, 3005, 2989, 1794, 1765, 1734, 1716, 1683, 1616, 1560, 1521, 1490, 1458, 1398, 1261 cm^{-1}; HRMS (ESI$^+$) calc. for $C_{31}H_{28}NO_5S$ [M + H]$^+$: 526.1683, found: 526.1696.

2-(2-Benzoyl-1-tosylindolin-3-yl)-1-(3-methoxyphenyl)ethan-1-one (3aah). White solid, yield = 93% (97.8 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08–7.97 (m, 2H), 7.69 (t, J = 8.3 Hz, 3H), 7.60 (t, J = 7.4 Hz, 1H), 7.49 (t, J = 7.7 Hz, 2H), 7.36–7.26 (m, 3H), 7.20 (d, J = 8.0 Hz, 3H), 7.10 (dd, J = 13.5, 5.0 Hz, 2H), 7.03 (t, J = 7.5 Hz, 1H), 5.36 (d, J = 3.4 Hz, 1H), 3.92–3.72 (m, 4H), 2.95 (dd, J = 17.8, 6.1 Hz, 1H), 2.58 (dd, J = 17.8, 7.8 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.87, 195.61, 160.02, 144.57, 141.63, 137.62, 135.16, 134.82, 133.74, 133.73, 130.01, 129.72, 129.34, 128.97, 128.83, 127.51, 125.11, 124.77, 120.66, 119.86, 116.16, 112.73, 69.84, 55.63, 45.02, 41.14, 21.67; IR (ATR): ν 3120, 3101, 3080, 3004, 2989, 1794, 1770, 1730, 1716, 1698, 1684, 1635, 1505, 1457, 1275, 1259 cm^{-1}; HRMS (ESI$^+$) calc. for $C_{31}H_{28}NO_5S$ [M + H]$^+$: 526.1683, found: 526.1689.

2-(2-Benzoyl-1-tosylindolin-3-yl)-1-(4-methoxyphenyl)ethan-1-one (3aai). White solid, yield = 95% (99.9 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07–7.96 (m, 2H), 7.71 (d, J = 8.3 Hz, 2H), 7.69–7.64 (m, 3H), 7.59 (t, J = 7.4 Hz, 1H), 7.48 (t, J = 7.7 Hz, 2H), 7.31–7.26 (m, 1H), 7.20 (d, J = 8.0 Hz, 2H), 7.09 (d, J = 7.5 Hz, 1H), 7.04–6.98 (m, 1H), 6.91–6.85 (m, 2H), 5.38 (d, J = 3.4 Hz, 1H), 3.91–3.85 (m, 4H), 2.93 (dd, J = 17.5, 6.2 Hz, 1H), 2.57 (dd, J = 17.5, 7.8 Hz, 1H), 2.36 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.62, 195.47, 163.94, 144.40, 141.61, 135.25, 134.80, 133.82, 133.68, 130.45, 129.96, 129.41, 129.33, 128.88, 128.80, 127.54, 125.14, 124.67, 115.98, 113.89, 69.92, 55.68, 44.51, 41.29, 21.74; IR (ATR): ν 3115, 3055, 3005, 2988, 2895, 1792, 1734, 1716, 1684, 1636, 1601, 1576, 1473, 1456, 1320, 1261 cm^{-1}; HRMS (ESI$^+$) calc. for $C_{31}H_{28}NO_5S$ [M + H]$^+$: 526.1683, found: 526.1690.

2-(2-Benzoyl-1-tosylindolin-3-yl)-1-(naphthalen-2-yl)ethan-1-one (3aaj). White solid, yield = 94% (102.6 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (s, 1H), 8.14–8.00 (m, 2H), 7.89 (dd, J = 15.0, 8.3 Hz, 3H), 7.81 (dd, J = 8.6, 1.6 Hz, 1H), 7.72 (d, J = 8.3 Hz, 2H), 7.68 (d, J = 8.1 Hz, 1H), 7.66–7.54 (m, 3H), 7.50 (t, J = 7.7 Hz, 2H), 7.29 (t, J = 7.8 Hz, 1H), 7.20–7.10 (m, 3H), 7.08–6.98 (m, 1H), 5.45 (d, J = 3.5 Hz, 1H), 4.01–3.87 (m, 1H), 3.17 (dd, J = 17.7, 6.0 Hz, 1H), 2.77 (dd, J = 17.7, 8.0 Hz, 1H), 2.26 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.03, 195.70, 144.50, 141.67, 135.86, 135.25, 134.85, 133.74, 133.71, 133.62, 132.51, 129.95, 129.66, 129.40, 128.99, 128.97, 128.84, 128.70, 128.62, 127.99, 127.57, 127.19, 125.12, 124.70, 123.66, 116.00, 69.90, 44.95, 41.29, 21.68; IR (ATR): ν 3095, 3052, 3005, 2988, 1790, 1770, 1750, 1735, 1686, 1652, 1575, 1540, 1507, 1485, 1457, 1419, 1362, 1262 cm^{-1}; HRMS (ESI$^+$) calc. for $C_{34}H_{28}NO_4S$ [M + H]$^+$: 546.1735, found: 546.1731.

1-([1,1′-Biphenyl]-4-yl)-2-(2-benzoyl-1-tosylindolin-3-yl)ethan-1-one (3aak). White solid, yield = 96% (109.8 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, J = 7.3 Hz, 2H), 7.77 (d, J = 8.4 Hz, 2H), 7.71 (dd, J = 14.9, 8.2 Hz, 3H), 7.68–7.58 (m, 5H), 7.49 (td, J = 7.9, 1.7 Hz, 4H), 7.42 (t, J = 7.3 Hz, 1H), 7.29 (t, J = 7.8 Hz, 1H), 7.21 (d, J = 8.1 Hz, 2H), 7.12 (d, J = 7.4 Hz, 1H), 7.04 (t, J =

7.5 Hz, 1H), 5.41 (d, J = 3.4 Hz, 1H), 3.99–3.87 (m, 1H), 3.01 (dd, J = 17.7, 6.1 Hz, 1H), 2.63 (dd, J = 17.7, 7.8 Hz, 1H), 2.36 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.59, 195.61, 146.39, 144.45, 141.62, 139.70, 135.20, 134.92, 134.80, 133.73, 133.71, 129.99, 129.33, 129.17, 128.94, 128.82, 128.72, 128.60, 127.52, 127.36, 127.35, 125.12, 124.75, 116.09, 69.83, 44.89, 41.16, 21.74; IR (ATR): ν 3145, 3095, 3005, 2991, 1791, 1772, 1731, 1719, 1617, 1545, 1501, 1473, 1420, 1360, 1261 cm^{-1}; HRMS (ESI^+) calc. for $C_{36}H_{30}NO_4S$ $[M + H]^+$: 572.1890, found: 572.1896.

2-(2-Benzoyl-1-tosylindolin-3-yl)-1-(furan-2-yl)ethan-1-one (3aal). White solid, yield = 89% (86.4 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04–7.98 (m, 2H), 7.74 (d, J = 8.3 Hz, 2H), 7.64 (d, J = 8.1 Hz, 1H), 7.61–7.56 (m, 1H), 7.52 (d, J = 1.0 Hz, 1H), 7.46 (t, J = 7.8 Hz, 2H), 7.27 (dd, J = 11.9, 3.7 Hz, 1H), 7.23 (d, J = 8.0 Hz, 2H), 7.07 (d, J = 7.5 Hz, 1H), 7.04–6.97 (m, 2H), 6.50 (dd, J = 3.6, 1.7 Hz, 1H), 5.45 (d, J = 3.5 Hz, 1H), 3.82 (td, J = 7.2, 3.4 Hz, 1H), 2.87 (dd, J = 17.1, 6.4 Hz, 1H), 2.54 (dd, J = 17.1, 7.9 Hz, 1H), 2.36 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.36, 186.09, 152.28, 146.81, 144.48, 141.53, 135.25, 134.61, 133.71, 133.14, 129.92, 129.21, 128.97, 128.82, 127.52, 125.11, 124.55, 117.73, 115.71, 112.58, 69.78, 44.39, 40.97, 21.69; IR (ATR): ν 3100, 3078, 2989, 1790, 1771, 1732, 1701, 1686, 1673, 1634, 1616, 1607, 1540, 1498, 1472, 1419, 1395, 1262 cm^{-1}; HRMS (ESI^+) calc. for $C_{28}H_{24}NO_5S$ $[M + H]^+$: 486.1370, found: 486.1356.

2-(2-Benzoyl-1-tosylindolin-3-yl)-1-(thiophen-2-yl)ethan-1-one (3aam). White solid, yield = 87% (87.3 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04–7.97 (m, 2H), 7.74 (d, J = 8.3 Hz, 2H), 7.68–7.63 (m, 2H), 7.61–7.55 (m, 1H), 7.47 (t, J = 7.7 Hz, 2H), 7.37 (dd, J = 3.8, 1.0 Hz, 1H), 7.27 (s, 1H), 7.23 (d, J = 8.4 Hz, 2H), 7.11–7.06 (m, 2H), 7.01 (dd, J = 7.9, 7.1 Hz, 1H), 5.44 (d, J = 3.3 Hz, 1H), 3.85 (td, J = 7.1, 3.4 Hz, 1H), 2.90 (dd, J = 17.0, 6.4 Hz, 1H), 2.62 (dd, J = 17.0, 7.7 Hz, 1H), 2.38 (d, J = 8.7 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.33, 189.84, 144.49, 143.58, 141.59, 135.33, 134.60, 134.54, 133.76, 133.23, 132.38, 129.99, 129.26, 129.04, 128.86, 128.25, 127.55, 125.15, 124.64, 115.87, 69.82, 45.23, 41.35, 21.72; IR (ATR): ν 3133, 3096, 3006, 2989, 1792, 1772, 1734, 1717, 1699, 1684, 1653, 1617, 1559, 1541, 1507, 1489, 1457, 1361, 1262 cm^{-1}; HRMS (ESI^+) calc. for $C_{28}H_{24}NO_4S_2$ $[M + H]^+$: 502.1141, found: 502.1152.

1-(2-Benzoyl-1-tosylindolin-3-yl)-3,3-dimethylbutan-2-one (3aan). White solid, yield = 89% (84.7 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00–7.92 (m, 2H), 7.73 (d, J = 8.2 Hz, 2H), 7.65 (d, J = 8.1 Hz, 1H), 7.59 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 7.7 Hz, 2H), 7.26 (dd, J = 11.5, 5.0 Hz, 3H), 7.03–6.94 (m, 2H), 5.18 (d, J = 3.7 Hz, 1H), 3.76 (td, J = 6.8, 3.8 Hz, 1H), 2.48–2.29 (m, 5H), 0.94 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.71, 195.38, 144.53, 141.55, 135.26, 134.70, 133.69, 133.52, 129.96, 129.15, 128.94, 128.85, 127.59, 125.17, 124.56, 115.75, 70.66, 44.10, 43.23, 40.95, 26.07, 21.70; IR (ATR): ν 3065, 3007, 2990, 1798, 1771, 1752, 1731, 1685, 1616, 1595, 1540, 1477, 1415, 1362, 1266 cm^{-1}; HRMS (ESI^+) calc. for $C_{28}H_{30}NO_4S$ $[M + H]^+$: 476.1890, found: 476.1905.

1-(2-Benzoyl-1-tosylindolin-3-yl)propan-2-one (3aao). White solid, yield = 87% (75.4 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, J = 8.2 Hz, 1H), 7.63 (d, J = 8.0 Hz, 2H), 7.57 (t, J = 7.5 Hz, 3H), 7.43 (t, J = 7.8 Hz, 2H), 7.30 (t, J = 7.6 Hz, 1H), 7.12–7.03 (m, 4H), 4.38 (d, J = 2.9 Hz, 1H), 3.99–3.89 (m, 1H), 2.72 (dd, J = 18.2, 5.8 Hz, 1H), 2.50 (s, 3H), 2.29 (s, 3H), 2.06 (dd, J = 18.2, 8.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.60, 196.98, 144.67, 140.87, 136.19, 134.36, 134.33, 133.63, 130.02, 128.92, 128.73, 128.00, 127.49, 125.42, 125.12, 117.22, 73.70, 44.60, 39.02, 27.09, 21.68; IR (ATR): ν 3065, 3008, 2996, 1793, 1760, 1756, 1733, 1685, 1616, 1595, 1541, 1476, 1420, 1362, 1261 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{25}H_{24}NO_4S$: 434.1421; found: 434.1430.

Procedure for the synthesis of 1,4-diphenyl-3,10-dihydro-[1,2]diazepino[4,5-*b*]indole 4aaa. A solution of DHI **3aaa** (99.1 mg, 0.2 mmol) in ethyl acetate (1 ml) was added to 24% aq. solution of hydrazine hydrate (19.2 mg, 0.6 mmol). The biphasic solution was vigorously stirred at 95 °C for 30 h. The reaction was monitored by TLC. After the complete consumption of reactant **3aaa**, ethyl acetate was added and the organic phase was separated and dried over Na_2SO_4. The organic phase was evaporated under reduced pressure and the crude product was purified using flash chromatography with hexane/ethyl acetate (5 : 1) as eluents and silica gel (100–200 mesh) as the stationary solid phase. The product **4aaa** was obtained as an off-white solid (56.2 mg, 79%).

1,4-Diphenyl-3,10-dihydro-[1,2]diazepino[4,5-*b*]indole (4aaa). White solid, yield = 79% (53.0 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (s, 1H), 8.02–7.96 (m, 2H), 7.95–7.88 (m, 3H), 7.53–7.47 (m, 3H), 7.43–7.34 (m, 5H), 7.35–7.27 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.08, 148.97, 138.17, 137.25, 136.40, 130.48, 129.93, 129.29, 129.16, 128.98, 128.81, 127.64, 127.19, 125.24, 124.15, 120.78, 119.30, 119.05, 112.19; IR (ATR): ν 3310, 3188, 3102, 3006, 1684, 1653, 1636, 1559, 1521, 1507, 1474, 1419, 1362, 1276 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{23}H_{18}N_3$: 336.1495; found: 336.1497.

***tert*-Butyl (2-(2,3-dibenzoylcyclopropyl)phenyl)carbamate (6aaa′).** White solid, yield = 42% (37.1 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (d, J = 8.1 Hz, 1H), 8.02–8.00 (m, 4H), 7.58–7.53 (m, 2H), 7.51 (s, 1H), 7.44 (t, J = 7.8 Hz, 4H), 7.34–7.28 (m, 1H), 7.23 (d, J = 7.6 Hz, 1H), 7.04 (td, J = 7.5, 1.0 Hz, 1H), 3.37–3.31 (m, 3H), 1.46 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.67, 153.12, 138.65, 136.77, 133.48, 128.71, 128.48, 128.36, 126.67, 125.78, 122.67, 119.79, 80.36, 77.28, 77.03, 76.77, 34.94, 28.23, 27.30; HRMS (ESI^+) calc. for $C_{28}H_{28}NO_4^+$ $[M + H]^+$: 442.2013, found: 442.2010.

General procedure for the synthesis of product 8. The preformed sulfonium salt **1** (0.3 mmol) and *ortho*-hydroxychalcone **7** (0.2 mmol) were added to toluene (2 mL). After stirring the mixture for 5 min, Cs_2CO_3 (65.2 mg, 0.2 mmol) was added and stirring was continued at rt. The progress of the reaction was monitored by TLC. After the completion of the reaction, the crude product **8** was purified by flash column chromatography on a silica support (hexane/ethyl acetate = 5 : 1).

2-(2-Benzoyl-2,3-dihydrobenzofuran-3-yl)-1-phenylethan-1-one (8aaa). White solid, yield = 94% (64.4 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (d, J = 7.4 Hz, 2H), 7.96 (d, J = 7.4 Hz, 2H), 7.66–7.53 (m, 2H), 7.52–7.44 (m, 4H), 7.23 (d, J = 7.4 Hz, 1H), 7.17 (t, J = 7.7 Hz, 1H), 6.95–6.82 (m, 2H), 5.66 (d, J = 5.5 Hz,

1H), 4.56 (dd, J = 13.5, 5.9 Hz, 1H), 3.64 (dd, J = 17.7, 6.0 Hz, 1H), 3.44 (dd, J = 17.7, 8.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.89, 194.90, 158.74, 136.56, 135.13, 133.70, 133.65, 129.52, 128.98, 128.86, 128.79, 128.25, 124.93, 121.55, 110.11, 87.78, 77.41, 77.16, 76.91, 44.23, 39.76; IR (ATR): ν 3050, 3003, 2991, 1731, 1686, 1650, 1600, 1580, 1555, 1541, 1506, 1473, 1443, 1280, 1258, 1210 cm^{-1}; HRMS (ESI$^+$) calc. for $C_{23}H_{19}O_3^+$ $[M + H]^+$: 343.1329, found: 343.1320.

2-(2-Benzoyl-5,7-di-*tert*-butyl-2,3-dihydrobenzofuran-3-yl)-1-phenylethan-1-one (8aba). White solid, yield = 89% (80.9 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15–8.07 (m, 2H), 8.02–7.90 (m, 2H), 7.61–7.55 (m, 2H), 7.47 (dd, J = 16.2, 8.1 Hz, 4H), 7.15 (d, J = 1.9 Hz, 1H), 7.13–7.07 (m, 1H), 5.62 (d, J = 5.3 Hz, 1H), 4.54–4.50 (m, 1H), 3.63 (dd, J = 17.5, 5.5 Hz, 1H), 3.45 (dd, J = 17.5, 8.6 Hz, 1H), 1.30 (s, 9H), 1.29 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.33, 195.40, 154.17, 144.19, 136.80, 135.26, 133.50, 133.46, 132.57, 129.56, 128.82, 128.71, 128.62, 128.29, 122.85, 119.19, 87.96, 77.41, 77.16, 76.91, 44.44, 39.60, 34.71, 34.37, 31.92, 29.51; IR (ATR): ν 3101, 3064, 2992, 1830, 1790, 1778, 1730, 1715, 1665, 1639, 1620, 1577, 1541, 1503, 1485, 1472, 1421, 1341, 1230 cm^{-1}; HRMS (ESI$^+$) calc. for $C_{31}H_{35}O_3^+$ $[M + H]^+$: 455.2581, found: 455.2579.

2-(2-Benzoyl-2,3-dihydrobenzofuran-3-yl)-1-(naphthalen-1-yl) ethan-1-one (8aab). White solid, yield = 91% (71.4 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.64 (d, J = 8.5 Hz, 1H), 8.20–8.06 (m, 2H), 8.01 (d, J = 8.2 Hz, 1H), 7.93–7.86 (m, 2H), 7.66–7.45 (m, 6H), 7.27 (d, J = 6.0 Hz, 1H), 7.18 (t, J = 7.7 Hz, 1H), 6.90 (dd, J = 17.2, 7.8 Hz, 2H), 5.74 (d, J = 5.6 Hz, 1H), 4.64 (dd, J = 13.4, 6.2 Hz, 1H), 3.71 (dd, J = 17.5, 6.1 Hz, 1H), 3.56 (dd, J = 17.5, 7.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 201.71, 195.07, 158.78, 135.19, 134.99, 134.15, 133.73, 133.53, 130.28, 129.53, 129.01, 128.93, 128.82, 128.63, 128.42, 128.40, 126.74, 125.91, 124.94, 124.44, 121.60, 110.16, 87.81, 77.41, 77.16, 76.91, 47.19, 40.33; IR (ATR): ν 3001, 2878, 2832, 1850, 1750, 1725, 1710, 1684, 1640, 1520, 1475, 1460, 1268 cm^{-1}; HRMS (ESI$^+$) calc. for $C_{27}H_{21}O_3^+$ $[M + H]^+$: 393.1485, found: 393.1489.

1-(2-Benzoyl-2,3-dihydrobenzofuran-3-yl)propan-2-one (8aac). White solid, yield = 87% (48.7 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (dd, J = 8.3, 1.2 Hz, 2H), 7.64–7.57 (m, 1H), 7.49 (dd, J = 10.8, 4.7 Hz, 2H), 7.19–7.13 (m, 2H), 6.93–6.82 (m, 2H), 5.54 (d, J = 5.8 Hz, 1H), 4.35 (dd, J = 13.5, 6.4 Hz, 1H), 3.08 (dd, J = 17.7, 6.3 Hz, 1H), 2.90 (dd, J = 17.7, 7.8 Hz, 1H), 2.19 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.60, 195.04, 158.62, 135.03, 133.76, 129.46, 128.98, 128.80, 128.72, 124.73, 121.55, 110.10, 87.65, 77.41, 77.16, 76.91, 48.76, 39.55, 30.37; IR (ATR): ν 3174, 3140, 3068, 3008, 2984, 2955, 1796, 1769, 1738, 1710, 1670, 1635, 1592, 1541, 1449, 1278 cm^{-1}; HRMS (ESI$^+$) calc. for $C_{18}H_{17}O_3^+$ $[M + H]^+$: 281.1172, found: 281.1179.

2-(2-(4-Bromobenzoyl)-2,3-dihydrobenzofuran-3-yl)-1-phenylethan-1-one (8daa). White solid, yield = 92% (77.5 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23–7.80 (m, 4H), 7.58 (q, J = 7.2 Hz, 1H), 7.51–7.39 (m, 4H), 7.23 (t, J = 6.5 Hz, 1H), 7.17 (q, J = 7.1 Hz, 1H), 6.94–6.90 (m, 1H), 6.89–6.80 (m, 1H), 5.59 (d, J = 5.5 Hz, 1H), 4.60–4.49 (m, 1H), 3.64 (dt, J = 17.8, 6.2 Hz, 1H), 3.48–3.36 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.94, 193.84, 158.55, 140.20, 136.48, 133.73, 133.51, 131.01, 129.12, 129.04, 128.90, 128.86, 128.24, 124.86, 121.68, 110.13, 87.78, 77.41, 77.16, 76.91, 44.14, 39.61; IR (ATR): ν 3060, 3002, 2991, 1777, 1760, 1734, 1710, 1684, 1598, 1560, 1510, 1479, 1431, 1276, 1228 cm^{-1}; HRMS (ESI$^+$) calc. for $C_{23}H_{17}BrO_3^+$ $[M]^+$: 420.0361, found: 420.0357.

Conflicts of interest

There are no conflicts to declare.

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