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Oxidative bicyclization of *N*-tethered 1,7-enynes toward polycyclic 3,4-dihydroquinolin-2(1*H*)-ones *via* site-selective decarboxylative C(sp^3)–H functionalization†

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A new Ag-catalyzed oxidative bicyclization of *N*-tethered 1,7-enynes with alkylcarboxylic acids for forming 41 examples of polycyclic 3,4-dihydroquinolin-2(1*H*)-ones has been established using readily accessible $K_2S_2O_8$ as an oxidant. The reaction pathway involves a silver-catalyzed decarboxylation/*in situ*-generated C-center radical-triggered α,β-conjugated addition/6-*exo*-*dig* cyclization/H-abstraction/5-*endo*-*trig* cyclization/SET sequence, allowing direct site-selective decarboxylative C(sp^3)–H functionalization toward the formation of multiple C–C bonds and rapid construction of complex spiroheterocycles.

Introduction

Molecules containing all-carbon quaternary stereocenters are ubiquitously distributed in natural products and bioactive substances, which have been found to exhibit a variety of biological and pharmacological activities.[1] Accordingly, the construction of sterically restricted quaternary stereocenters has attracted the interest of synthetic chemists because of their special structural features and their tendency to tightly bind to target molecules.[2] As a result, numerous efforts have been devoted to develop efficient methodologies for their direct construction,[3] which generally involved pericyclic,[4] alkylation,[5] photochemical,[6] transition metal-catalyzed,[7] radical,[8] and semi-pinacol rearrangement reactions.[9] Among which, oxidative radical reactions have been proved to be a high-efficient synthetic strategy toward these molecules contained all-carbon quaternary stereocenters.[10] For instance, Nevado and co-workers reported radical-triggered aryl migration strategies to construct all-carbon quaternary stereocenters *via* desulfonylative bi-functionalization of *N*-aryl-*N*-arylsulfonyl methacrylamides.[11] However, to the best of our knowledge, catalytic decarboxylative C(sp^3)–H functionalization for the construction of spiro-quaternary stereocenters through radical-triggered bicyclization is virtually unexplored.

1,7-Enynes are types of competent reactants endowed with multiple reactive sites, which could be used as versatile and synthetically useful feedstocks for the construction of molecules containing multiple functionalities.[12] Specifically, oxidative radical 1,7-enyne-cyclizations have gradually become a powerful platform for rapid collection of cyclic compounds with all-carbon quaternary stereocenters *via* synergistic processes across the C=C and C≡C bond systems in a single step fashion.[13] These reactions feature annulation efficiency, extreme convergence while minimizing the generation of waste. Recently, we reported the addition of various C-centered radicals to *N*-tethered 1,7-enynes, which underwent a radical addition–cyclization/H-abstraction/radical coupling sequence to access spiro-fused cyclopenta[*c*]quinolones (Scheme 1a).[14] Meanwhile, Li and co-workers presented a metal-free radical [2 + 2 + 1] carbocyclization reaction of *N*-tethered 1,7-enynes with two C(sp^3)–H bonds adjacent to a heteroatom to build similar spirocyclic compounds (Scheme 1b), but only trace amount of spirocyclic compound was observed when R is a strong electron-withdrawing Ts group.[15] For this reaction, we attempted to employ *N*-Ts tethered 1,7-enyne **1a** to react with 2,3-dihydrobenzo[*b*][1,4]dioxine under the above reported conditions.[14,15] Unluckily, the reaction hardly proceeded with observation of trace amount of the expected product **3a** as most of the starting materials remained unreacted. These unsatisfactory results led us to change synthetic strategy for spiro-fused 3,4-dihydroquinolin-2(1*H*)-one preparation.[16] A survey revealed that decarboxylative coupling reactions have become a powerful tool for the collection of functionalized molecules through direct carbon–carbon bond formation.[17] Considering Ag-catalyzed decarboxylation often trapped by a radical process,[17] we envisaged that 2,3-dihydrobenzo[*b*][1,4]dioxine-2-carboxylic acid as a potential radical donor was

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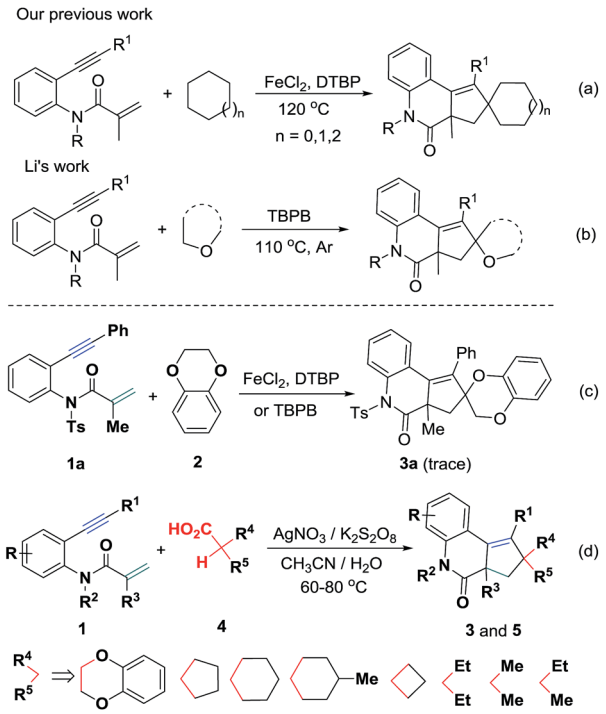


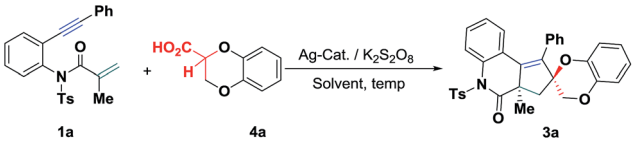
Scheme 1 Cascade bicyclization of 1,7-enynes.

subjected to the reaction with *N*-Ts tethered 1,7-enynes in Ag-catalysis, enabling decarboxylative C(sp^3)–H functionalization to access the expected spiro-fused 3,4-dihydroquinolin-2(1*H*)-ones. Herein, we report the successful implementation of this idea with these special and practical transformations in which a wide range of spiro-fused 3,4-dihydroquinolin-2(1*H*)-ones **3** were achieved through Ag-catalyzed decarboxylative bicyclizations of *N*-tethered 1,7-enynes **1** and 2,3-dihydrobenzo[*b*][1,4]dioxine-2-carboxylic acid **4a**. Using cycloalkyl- (*e.g.* cyclopentyl **4b**, cyclohexyl **4c**, 4-methylcyclohexyl **4d**, cyclobutyl **4e**) and alkyl-substituted (*e.g.* pentan-3-yl **4f**, isopropyl **4g**, and *sec*-butyl **4h**) carboxylic acids as radical donors to expand the synthetic utility of this methodology, the reaction smoothly proceeds through a similar decarboxylative bicyclizations, delivering a series of important fused 3,4-dihydroquinolin-2(1*H*)-ones **5** with two quaternary stereocenters. To the best of our knowledge, this is the first site-selective decarboxylative C(sp^3)–H functionalization of alkylcarboxylic acids for the assemble of these special polycyclic 3,4-dihydroquinolin-2(1*H*)-ones with excellent diastereoselectivity through an oxidative silver-catalysis.

Results and discussion

Our initial investigation was started with the treatment of *N*-Ts tethered 1,7-enyne **1a** (1.0 equiv.) by 2,3-dihydrobenzo[*b*][1,4]dioxine-2-carboxylic acid (**4a**, 2.0 equiv.) under air conditions in a 1 : 1 ratio of MeCN–H_2O mixture at 80 °C. The reaction in the presence of $AgNO_3$ (20 mol%) and $K_2S_2O_8$ (4.0 equiv.) led to the selective formation of the expected product **3a** as a sole diastereoisomer in 48% yield (dr > 99 : 1 established on the basis of ^{1}H NMR) (Table 1, entry 1). Lowering the loading of

Table 1 Optimization of the reaction conditions[a]

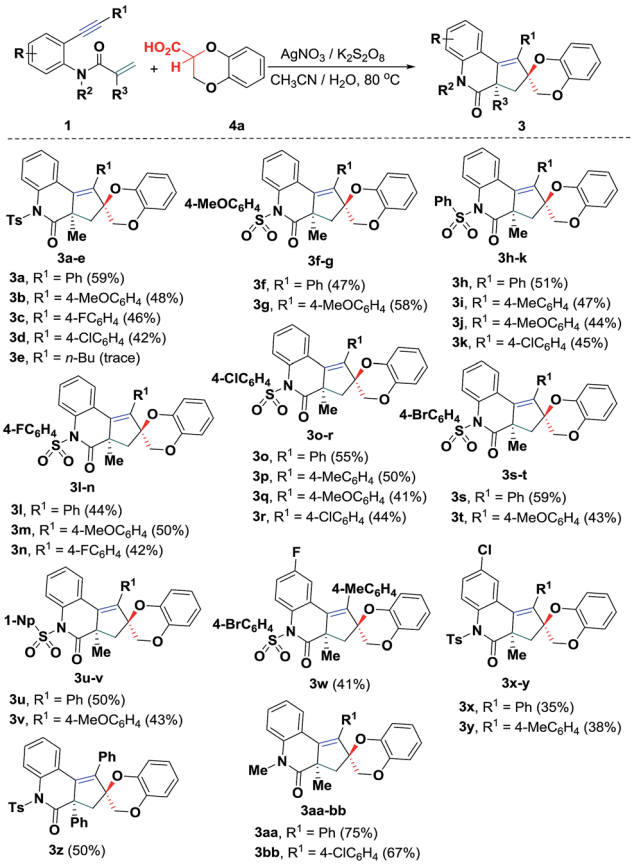


Entry	Ag-Cat. (mol%)	Solvent	*t* (°C)	Yield[b] (%)
1	$AgNO_3$ (20)	CH_3CN/H_2O (1 : 1)	80	48
2	$AgNO_3$ (10)	CH_3CN/H_2O (1 : 1)	80	59
3[c]	$AgNO_3$ (10)	CH_3CN/H_2O (1 : 1)	80	26
4	$AgNO_3$ (10)	CH_3CN/H_2O (1 : 1)	100	37
5[d]	$AgNO_3$ (10)	CH_3CN/H_2O (1 : 1)	80	47
6	$AgNO_3$ (10)	CH_3CN/H_2O (4 : 1)	80	N.D.
7	AgOAc (10)	CH_3CN/H_2O (1 : 1)	80	25
8	Ag_2CO_3 (10)	CH_3CN/H_2O (1 : 1)	80	Trace
9	$AgNTf_2$ (10)	CH_3CN/H_2O (1 : 1)	80	33
10	AgOTf (10)	CH_3CN/H_2O (1 : 1)	80	Trace
11	AgF (10)	CH_3CN/H_2O (1 : 1)	80	30
12	$AgNO_3$ (10)	DCE/H_2O (1 : 1)	80	N.D.
13	$AgNO_3$ (10)	THF/H_2O (1 : 1)	80	N.D.
14	$AgNO_3$ (10)	1,4-Dioxane/H_2O (1 : 1)	80	25
15	$AgNO_3$ (10)	Acetone/H_2O(1 : 1)	80	N.D.
16	—	CH_3CN/H_2O (1 : 1)	80	N.R.

[a] Reaction conditions: **1a** (0.20 mmol), **4a** (0.4 mmol), Ag-catalyst (*x* mol%) $K_2S_2O_8$ (0.8 mmol), mixed solvent (4 mL), 80 °C, air conditions. [b] Isolated yield based on substrate **1** by column chromatography. [c] Using 1.0 mmol of $K_2S_2O_8$. [d] The ratio of **1a** and **4a** was in 1 : 2.5. N.D. = no detected. N.R. = no reaction.

$AgNO_3$ to 10 mol% gave a higher yield of 59% (entry 2). In contrast, increasing the dosage of $K_2S_2O_8$ to 5.0 equivalents resulted in an inferior outcome (entry 3). The relatively lower conversion into **3a** was detected when temperature was elevated to 100 °C (entry 4) whereas fine-tuning the ratio of **1a** with **4a** to 1 : 2.5 still decreased the yield of **3a** (entry 5). The use of 4 : 1 mixture of MeCN and H_2O completely suppressed the reaction process (entry 6). As the next optimization step, we performed the screening of a variety of silver salts, including AgOAc, Ag_2CO_3, $AgNTf_2$, AgOTf, and AgF, for this bicyclization at 80 °C by using 4.0 equiv. of $K_2S_2O_8$ as an oxidant (entries 7–11). Unfortunately, all of these silver catalysts did not show higher catalytic activity than $AgNO_3$. Changing mixed solvents of 1,2-dichloroethane (DCE)–H_2O, tetrahydrofuran (THF)–H_2O, 1,4-dioxane–H_2O, and acetone–H_2O revealed that all these media cannot further enhance yields (entries 12–15). Without $AgNO_3$, the reaction did not work under oxidative conditions (entry 16).

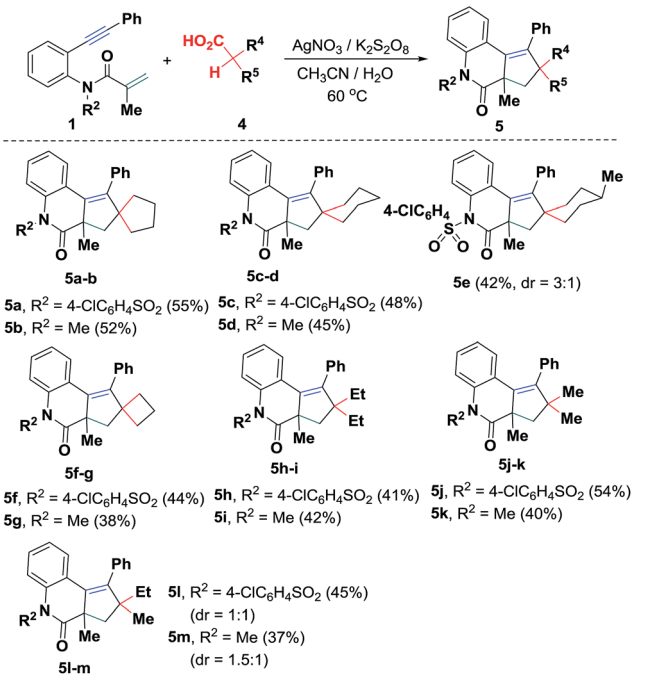
With the established optimal conditions (Table 1, entry 2), we set out to investigate the generality of this silver-catalyzed oxidative bicyclization by using a variety of *N*-tethered 1,7-enynes. We found that various substituents on the aromatic ring of both the alkynyl (R^1) and sulfonyl (R^2) moieties were proven not to hamper this Ag-catalysis, and a wide range of diastereoenriched spiro-fused 3,4-dihydroquinolin-2(1*H*)-ones **3a–3bb** with structural diversity can be afforded in acceptable yields and a functional-group-compatible fashion (dr > 99 : 1 established on the basis of ^{1}H NMR, Scheme 2). For instance, with the Ts protection group (R^2) on the amine anchor, the variant of substituents on the



Scheme 2 Domino synthesis of spiro-fused quinolin-2(1*H*)-ones **3**. (a) Isolated yields based on 1,7-enynes **1** by column chromatography. (b) 1,7-Enynes **1** (0.20 mmol), **4a** (0.4 mmol), $AgNO_3$ (0.020 mol), $K_2S_2O_8$ (0.8 mmol), and CH_3CN–H_2O (4.0 mL), at 80 °C for 12 hours.

arylalkynyl moiety, including MeO, F, and Cl can tolerate the catalytic conditions well. Electronic effect of substituents on the arylalkynyl moiety seems to show no impact on the reaction efficiency. However, *n*-butyl substituted 1,7-enyne **1e** was not a good component for this reaction (Scheme 2, **3e**), which may be ascribed to the relative instability of the vinyl radical intermediate (Scheme 2) generated *in situ* from C-centered radical triggered addition/6-*exo*-*dig* cyclization. Next, electronic nature of substituents on both *N*-arylalkynyl (R^1) and arylsulfonyl (R^2) moieties was probed. The reaction occurred smoothly with a variety of functional groups on both *N*-arylsulfonyl and arylalkynyl moieties of substrates **1**. Various functional groups including methoxy, methyl, fluoride, chloride, and bromide at the para-positions of the aromatic ring directly bound to *N*-arylsulfonyl and/or arylalkynyl moieties were well tolerated under this system, delivering the corresponding spirocyclic cyclopenta[*c*]quinolines **3f–3t** with yields ranging from 41% to 59%. Alternatively, sterically encumbered 1-naphthalenyl (1-Np) analogues **1u–1v** were successfully engaged in the current bicyclization transformations, giving access to the corresponding cyclopenta[*c*]quinolines **3u–3v** in moderate yields. The presence of both fluoro and chloro functionalities at C4 position of the internal arene rings of *N*-tethered 1,7-enynes proved to be more reluctant to undergo the reaction process, as diastereoenriched products **3w–3y** were obtained in 35–41% yields. Similarly, replacing methyl group with aryl substituent on the terminal olefin unit, *N*-tethered 1,7-enyne **1z** was a good reaction partner, enabling radical bicyclization to access product **3z** in 50% yield. Besides, *N*-methyl 1,7-enynes **1aa** and **1bb** would be accommodated, confirming the reaction efficiency, as **3aa** and **3bb** with high diastereopurity were generated in 75% and 67% yields, respectively.

After the successful utilization of various *N*-tethered 1,7-enynes **1** with carboxylic acid **4a**, we continued to explore this decarboxylative bicyclization by the adoption of other seven examples of representative cycloalkyl- and alkyl-substituted carboxylic acids **4b–h** as the coupling partner (Scheme 3). As we had expected, these reactions worked well to give access to the corresponding fused cyclopenta[*c*]quinoline products. Various cycloalkyl carboxylic acids including cyclopentyl **4b**, cyclohexyl **4c**, 4-methylcyclohexyl **4d**, and cyclobutyl **4e** could be efficiently converted into the corresponding spiro-fused 3,4-dihydroquinolin-2(1*H*)-ones **5a–g** with yields ranging from 38% to 55% yields. Similarly, alkylcarboxylic acids such as pentan-3-yl **4f**, isopropyl **4g** and *sec*-butyl **4h** can tolerate the catalytic oxidation conditions well. Among them, 4-methylcyclohexyl (**4d**) and *sec*-butyl (**4h**) counterparts delivered the desired diastereoselective isomers **5e** and **5l–5m**, respectively, albeit with moderate yields of 37–45%. It is noteworthy that the protocol provides a valuable pathway for the construction of fused cyclopenta[*c*]quinoline derivatives **5e** and **5h–m** in an atom-efficient fashion, which are normally difficult to synthesize by the previously reported methods.[14,15] The stereostructural elucidation of the products was confirmed by their NMR and HRMS spectra. In the cases of **3a** and **5j**, both structures were unequivocally determined by X-ray analysis (Fig. 1 and 2).



Scheme 3 Domino synthesis of fused quinolin-2(1*H*)-ones **5**. (a) Isolated yields based on 1,7-enynes **1** by column chromatography. (b) **1** (0.3 mmol), **4b–4h** (0.2 mmol), $AgNO_3$ (0.020 mol), $K_2S_2O_8$ (0.8 mmol), and CH_3CN–H_2O (4.0 mL), at 60 °C for 12 hours.

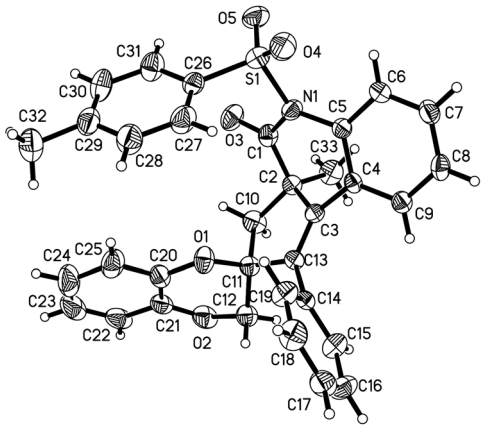


Fig. 1 X-ray structure of **3a**.

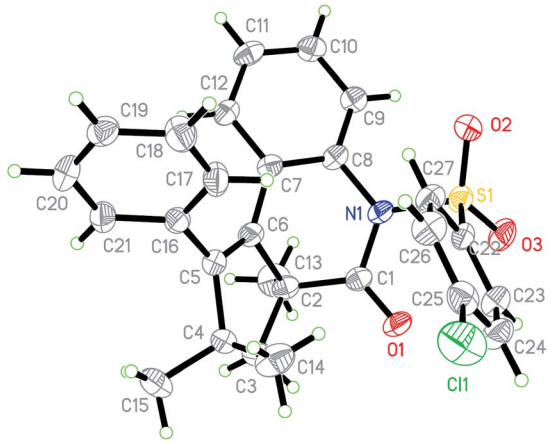
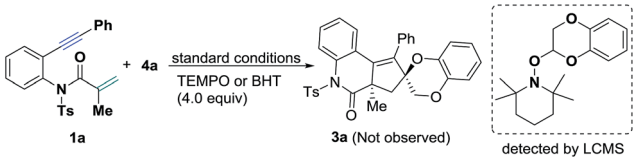


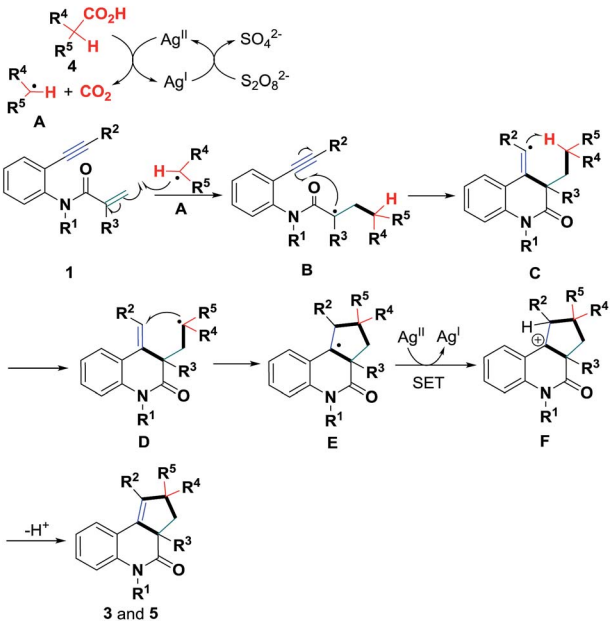
Fig. 2 X-ray structure of **5j**.

To gain mechanistic insight into this reaction, several control experiments were conducted. *N*-Tethered 1,7-enynes **1a** was subjected to reaction with 4.0 equivalents of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) or butylhydroxytoluene (BHT; Scheme 4), but no expected product **3a** was observed with the starting material **1a** remaining. For the former reaction, the TEMPO–2,3-dihydrobenzo[*b*][1,4]dioxine adduct was detected by LC-MS (MS = 291.2) analysis, which suggested that the reaction underwent a free-radical addition process, which is consistent with the mechanisms proposed in previous reports.[17]

On the basis of our own observations and literature survey,[13] a tentative mechanism is proposed in Scheme 5. The first step is to form the Ag(II) cation, derived from the oxidization of Ag(I) by the $S_2O_8^{2-}$, which captures a single electron from carboxylate



Scheme 4 Control experiments.



Scheme 5 Proposed mechanisms for forming products **3** and **5**.

and subsequent decarboxylation to produce the corresponding C-center radical **A**.[18] Then, the intermolecular α,β-conjugated addition of the resulting C-center radical **A** onto *N*-tethered 1,7-enynes **1**, followed by 6-*exo-dig* cyclization and H-abstraction affords alkyl radical intermediate **D**.[15] The intramolecular 5-*endo-trig* cyclization (the addition of C-center radical onto the double bond of intermediate **D**) occurs to generate radical intermediate **E**, which undergoes a single electron transfer (SET) and deprotonation to give the desired products **3** and **5**.

Conclusions

In conclusion, we have developed a C-center radical-triggered bicyclization of *N*-tethered 1,7-enynes with a large variety of functional groups that provides efficient construction of richly decorated ploycyclic cyclopenta[*c*]quinolines with two all-carbon quaternary stereocenters *via* a sequential silver-catalyzed decarboxylation/C-center radical-induced α,β-conjugated addition/6-*exo-dig* cyclization/H-abstraction/5-*endo-trig* cyclization/SET process. This transformation offers a valuable replenishment for constructing a series of spirocyclic cyclopenta[*c*]quinolones with high diastereoselectivity through site-selective decarboxylative C(sp^3)–H functionalization. The bond-forming/annulation efficiency, accessibility of starting materials, and functional group tolerance make this reaction a powerful synthetic tool with a great substrate scope. Further study on the scope extension of this reaction is currently underway in our laboratories.

Experiment

General information

All one-pot reactions were carried out in a 10 mL Schlenk tube equipped with a magnetic stir bar under air conditions. All

melting points are uncorrected. The NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 on a 400 MHz instrument with TMS as internal standard. Chemical shifts (δ) were reported in ppm with respect to TMS. Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiples), coupling constant (J, Hz) and integration. HRMS analyses were carried out using a TOF-MS instrument with an ESI source. X-ray crystallographic analysis was performed with a SMART CCD and a P4 diffractometer.

General procedure for the synthesis of product 3a

A mixture of *N*-(2-(phenylethynyl)phenyl)-*N*-tosylmethacrylamide (**1a**, 83 mg, 0.2 mmol 1.0 equiv.), 2,3-dihydrobenzo[*b*][1,4] dioxine-2-carboxylic acid (**2a**, 72 mg, 0.4 mmol, 2.0 equiv.), $AgNO_3$ (3.4 mg, 10 mol%) and $K_2S_2O_8$ (216 mg, 0.8 mmol 4.0 equiv.) in a mixed solvent of MeCN (2.0 mL) and H_2O (2.0 mL) was heated under air conditions at 80 °C for 12 hours. After completion of the reaction as indicated by TLC (petroleum ether: ethyl acetate 5 : 1), the reaction mixture was extracted with ethyl acetate and concentrated *in vacuo*. After that, the crude product was purified by flash column chromatography (silica gel, mixtures of petroleum ether/acetic ester, 50 : 1, v/v) to afford the desired pure product **3a**.

3*a*′-Methyl-1′-phenyl-5′-tosyl-3′,3*a*′-dihydro-3*H*-spiro[benzo[*b*][1,4]dioxine-2,2′-cyclopenta[*c*]quinolin]-4′(5′*H*)-one (3a). White solid, mp 215–216 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.85 (d, J = 8.4 Hz, 2H), 7.76 (d, J = 8.0 Hz, 1H), 7.40–7.33 (m, 6H), 7.23–7.21 (m, 2H), 7.09–7.05 (m, 1H), 7.02–7.00 (m, 1H), 6.80–6.74 (m, 3H), 6.54–6.50 (m, 1H), 4.12 (d, J = 10.8 Hz, 1H), 4.08 (d, J = 12.0 Hz, 1H), 2.51 (s, 3H), 2.44 (d, J = 14.4 Hz, 1H), 2.32 (d, J = 14.8 Hz, 1H), 1.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 174.09, 144.85, 142.35, 140.24, 139.06, 137.07, 136.56, 135.01, 132.78, 131.89, 129.46, 129.44, 129.42, 128.93, 128.63, 128.52, 128.33, 128.30, 127.87, 127.40, 126.33, 124.18, 124.13, 121.61, 121.17, 117.68, 116.80, 86.12, 69.90, 54.54, 43.90, 24.63, 21.77; IR (KBr, ν, cm^{-1}) 3046, 1716, 1652, 1558, 1494, 1360, 1265, 1166, 810, 755; HRMS (APCI-TOF) m/z calcd for: $C_{33}H_{28}NO_5S$, 550.1688 [M + H]$^+$; found: 550.1667.

1′-(4-Methoxyphenyl)-3*a*′-methyl-5′-tosyl-3′,3*a*′-dihydro-3*H*-spiro[benzo[*b*][1,4]dioxine-2,2′-cyclopenta[*c*]quinolin]-4′(5′*H*)-one (3b). White solid, mp 213–214 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.85 (d, J = 8.4 Hz, 2H), 7.76 (d, J = 8.4 Hz, 1H), 7.38–7.33 (m, 3H), 7.17–7.14 (m, 2H), 7.11–7.04 (m, 2H), 6.90–6.87 (m, 2H), 6.81–6.75 (m, 3H), 6.54–6.50 (m, 1H), 4.12 (d, J = 11.2 Hz, 1H), 4.09 (d, J = 10.8 Hz, 1H), 3.82 (s, 3H), 2.50 (s, 3H), 2.42 (d, J = 14.8 Hz, 1H), 2.31 (d, J = 14.8 Hz, 1H), 1.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 174.19, 159.52, 144.82, 142.36, 139.81, 138.76, 136.58, 135.04, 130.65, 129.45, 128.53, 128.49, 127.46, 126.31, 124.74, 124.42, 124.11, 121.61, 121.15, 117.71, 116.79, 113.84, 86.07, 69.95, 55.26, 54.34, 43.80, 30.96, 24.51, 21.76; IR (KBr, ν, cm^{-1}) 2974, 1722, 1645, 1574, 1471, 1361, 1248, 1118, 836, 747; HRMS (APCI-TOF) m/z calcd for: $C_{34}H_{30}NO_6S$, 580.1794 [M + H]$^+$; found: 580.1785.

1′-(4-Fluorophenyl)-3*a*′-methyl-5′-tosyl-3′,3*a*′-dihydro-3*H*-spiro[benzo[*b*][1,4]dioxine-2,2′-cyclopenta[*c*]quinolin]-4′(5′*H*)-one (3c). White solid, mp 184–186 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.88 (d, J = 8.0 Hz, 2H), 7.80 (d, J = 8.0 Hz, 1H), 7.41–7.37 (m, 3H), 7.24–7.20 (m, 2H), 7.13–7.05 (m, 3H), 7.03–7.01 (m, 1H), 6.83–6.77 (m, 3H), 6.56–6.54 (m, 1H), 4.13 (d, J = 10.8 Hz, 1H), 4.09 (d, J = 11.2 Hz, 1H), 2.53 (s, 3H), 2.49 (d, J = 13.6 Hz, 1H), 2.34 (d, J = 14.8 Hz, 1H), 1.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 173.98, 162.64 ($^1J_{CF}$ = 246.80 Hz), 144.92, 142.26 ($^4J_{CF}$ = 2.20 Hz), 140.76, 138.09, 136.55, 135.06, 131.26 ($^3J_{CF}$ = 8.10 Hz), 129.46, 128.80, 128.52, 127.32, 126.33, 124.12, 123.96, 121.70, 121.27, 117.59, 116.82, 115.48 ($^2J_{CF}$ = 21.40 Hz), 85.85, 69.63, 54.53, 43.94, 24.78, 21.64; IR (KBr, ν, cm^{-1}) 2977, 1716, 1699, 1598, 1494, 1361, 1264, 1169, 847, 772; HRMS (APCI-TOF) m/z calcd for: $C_{33}H_{27}NO_5SF$, 568.1594 [M + H]$^+$; found: 568.1561.

1′-(4-Chlorophenyl)-3*a*′-methyl-5′-tosyl-3′,3*a*′-dihydro-3*H*-spiro[benzo[*b*][1,4]dioxine-2,2′-cyclopenta[*c*]quinolin]-4′(5′*H*)-one (3d). White solid, mp 222–223 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.85 (d, J = 8.0 Hz, 2H), 7.77 (d, J = 8.4 Hz, 1H), 7.37 (d, J = 8.0 Hz, 3H), 7.33 (d, J = 8.4 Hz, 2H), 7.16 (d, J = 8.4 Hz, 2H), 7.11–7.08 (m, 1H), 6.99 (d, J = 7.6 Hz, 1H), 6.77–6.75 (m, 3H), 6.53–6.51 (m, 1H), 4.11 (d, J = 10.8 Hz, 1H), 4.07 (d, J = 10.8 Hz, 1H), 2.50 (s, 3H), 2.46 (d, J = 14.8 Hz, 1H), 2.32 (d, J = 14.8 Hz, 1H), 1.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 173.91, 144.95, 142.25, 142.18, 140.91, 137.81, 136.51, 135.05, 134.44, 131.24, 130.84, 129.46, 128.89, 128.64, 128.51, 127.32, 126.38, 124.13, 123.85, 121.73, 121.31, 117.59, 116.83, 86.04, 69.82, 54.57, 43.94, 24.56, 21.75; IR (KBr, ν, cm^{-1}) 2976, 1716, 1699, 1593, 1490, 1357, 1248, 1165, 833, 757; HRMS (APCI-TOF) m/z calcd for: $C_{33}H_{27}NO_5SCl$, 584.1298 [M + H]$^+$; found: 584.1278.

5′-((4-Methoxyphenyl)sulfonyl)-3*a*′-methyl-1′-phenyl-3′,3*a*′-dihydro-3*H*-spiro[*b*enzo[*b*][1,4]dioxine-2,2′-cyclopenta[*c*]quinolin]-4′(5′*H*)-one (3f). White solid, mp 178–179 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.93 (d, J = 8.8 Hz, 2H), 7.78 (d, J = 8.0 Hz, 1H), 7.40–7.35 (m, 4H), 7.25–7.23 (m, 2H), 7.11–7.02 (m, 4H), 6.83–6.77 (m, 3H), 6.60–6.57 (m, 1H), 4.14 (d, J = 10.8 Hz, 1H), 4.09 (d, J = 11.2 Hz, 1H), 3.95 (s, 3H), 2.48 (d, J = 14.8 Hz, 1H), 2.35 (d, J = 14.8 Hz, 1H), 1.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 174.20, 163.84, 142.37, 142.32, 140.34, 138.94, 135.04, 132.78, 131.01, 130.57, 129.44, 128.59, 128.31, 128.28, 127.33, 126.31, 124.30, 124.24, 121.62, 121.14, 117.77, 116.76, 113.97, 86.14, 69.93, 55.73, 54.62, 43.98, 24.69; IR (KBr, ν, cm^{-1}) 2971, 1715, 1683, 1594, 1495, 1372, 1264, 1186, 831, 781; HRMS (APCI-TOF) m/z calcd for: $C_{33}H_{28}NO_6S$, 566.1637 [M + H]$^+$; found: 566.1629.

1′-(4-Methoxyphenyl)-5′-((4-methoxyphenyl)sulfonyl)-3*a*′-methyl-3′,3*a*′-dihydro-3*H*-spiro[benzo[*b*][1,4]dioxine-2,2′-cyclopenta[*c*]quinolin]-4′(5′*H*)-one (3g). White solid, mp 201–203 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.90 (d, J = 8.8 Hz, 2H), 7.76 (d, J = 8.0 Hz, 1H), 7.37–7.32 (m, 1H), 7.15 (d, J = 8.8 Hz, 2H), 7.11–7.01 (m, 4H), 6.88 (d, J = 8.4 Hz, 2H), 6.81–6.75 (m, 3H), 6.58–6.55 (m, 1H), 4.09 (s, 2H), 3.92 (s, 3H), 3.81 (s, 3H), 2.42 (d, J = 14.4 Hz, 1H), 2.31 (d, J = 14.4 Hz, 1H), 1.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 174.30, 163.81, 159.50, 142.38, 142.36, 139.92, 138.64, 135.06, 130.98, 130.64, 130.60, 128.49, 127.39, 126.29, 124.74, 124.47, 124.27, 121.61, 121.13, 117.80, 116.75, 113.96, 113.82, 86.10, 69.98, 55.72, 55.26, 54.42, 43.89, 24.57; IR (KBr, ν, cm^{-1}) 2927, 1716, 1683, 1575, 1472, 1362,

1264, 1165, 834, 747; HRMS (APCI-TOF) *m*/*z* calcd for: $C_{34}H_{30}NO_7S$, 596.1743 $[M + H]^+$; found: 596.1744.

3*a*′-Methyl-1′-phenyl-5′-(phenylsulfonyl)-3′,3*a*′-dihydro-3*H*-spiro[benzo[*b*][1,4]dioxine-2,2′-cyclopenta[*c*]quinolin]-4′(5′*H*)-one (3h). White solid, mp 182–184 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.96 (d, J = 7.6 Hz, 2H), 7.77 (d, J = 8.4 Hz, 1H), 7.73–7.69 (m, 1H), 7.62–7.58 (m, 2H), 7.37–7.34 (m, 4H), 7.23–7.20 (m, 2H), 7.10–7.06 (m, 1H), 7.03–7.01 (m, 1H), 6.77–6.74 (m, 3H), 6.55–6.52 (m, 1H), 4.11 (d, J = 10.8 Hz, 1H), 4.06 (d, J = 11.2 Hz, 1H), 2.45 (d, J = 14.8 Hz, 1H), 2.31 (d, J = 14.8 Hz, 1H), 1.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 174.07, 142.31, 142.28, 140.05, 139.53, 139.17, 134.98, 133.76, 132.73, 129.41, 128.84, 128.66, 128.39, 128.32, 127.44, 126.43, 124.21, 124.15, 121.66, 121.15, 117.76, 116.74, 86.07, 69.90, 54.54, 43.81, 24.60; IR (KBr, ν, cm^{-1}) 2949, 1717, 1593, 1493, 1361, 1256, 1170, 1085, 837, 740; HRMS (APCI-TOF) *m*/*z* calcd for: $C_{32}H_{26}NO_5S$, 536.1532 $[M + H]^+$; found: 536.1513.

3*a*′-Methyl-5′-(phenylsulfonyl)-1′-(*p*-tolyl)-3′,3*a*′-dihydro-3*H*-spiro[benzo[*b*][1,4]dioxine-2,2′-cyclopenta[*c*]quinolin]-4′(5′*H*)-one (3i). White solid, mp 185–187 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.96 (d, J = 7.6 Hz, 2H), 7.77 (d, J = 8.4 Hz, 1H), 7.72–7.69 (m, 1H), 7.61–7.57 (m, 2H), 7.38–7.32 (m, 1H), 7.17 (d, J = 7.6 Hz, 2H), 7.12–7.05 (m, 4H), 6.79–6.74 (m, 3H), 6.54–6.52 (m, 1H), 4.08 (s, 2H), 2.42 (d, J = 14.8 Hz, 1H), 2.36 (s, 3H), 2.31 (d, J = 14.8 Hz, 1H), 1.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 174.15, 142.36, 142.32, 139.76, 139.56, 139.18, 138.15, 134.99, 133.72, 129.62, 129.26, 129.07, 128.84, 128.58, 128.38, 127.50, 126.42, 124.41, 124.16, 121.64, 121.12, 117.82, 116.73, 86.08, 69.94, 54.47, 43.74, 24.53, 21.28; IR (KBr, ν, cm^{-1}) 3086, 1716, 1683, 1576, 1489, 1387, 1262, 1086, 888, 750; HRMS (APCI-TOF) *m*/*z* calcd for: $C_{33}H_{28}NO_5S$, 550.1688 $[M + H]^+$; found: 550.1658.

1′-(4-Methoxyphenyl)-3*a*′-methyl-5′-(phenylsulfonyl)-3′,3*a*′-dihydro-3*H*-spiro[benzo[*b*][1,4]dioxine-2,2′-cyclopenta[*c*]quinolin]-4′(5′*H*)-one (3j). White solid, mp 204–205 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.96 (d, J = 7.6 Hz, 2H), 7.77 (d, J = 8.0 Hz, 1H), 7.72–7.68 (m, 1H), 7.60–7.56 (m, 2H), 7.38–7.34 (m, 1H), 7.17–7.07 (m, 4H), 6.88 (d, J = 8.4 Hz, 2H), 6.79–6.75 (m, 3H), 6.55–6.53 (m, 1H), 4.09 (s, 2H), 3.82 (s, 3H), 2.42 (d, J = 14.8 Hz, 1H), 2.31 (d, J = 14.8 Hz, 1H), 1.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 174.18, 159.54, 142.34, 139.65, 139.57, 138.89, 135.01, 133.74, 130.63, 128.84, 128.57, 128.37, 127.51, 126.41, 124.71, 124.46, 124.14, 121.67, 121.15, 117.80, 116.75, 113.85, 86.04, 69.96, 55.26, 54.35, 43.73, 24.49; IR (KBr, ν, cm^{-1}) 3039, 1717, 1675, 1569, 1490, 1395, 1339, 1174, 833, 668; HRMS (APCI-TOF) *m*/*z* calcd for: $C_{33}H_{28}NO_6S$, 566.1637 $[M + H]^+$; found: 566.1615.

1′-(4-Chlorophenyl)-3*a*′-methyl-5′-(phenylsulfonyl)-3′,3*a*′-dihydro-3*H*-spiro[benzo[*b*][1,4]dioxine-2,2′-cyclopenta[*c*]quinolin]-4′(5′*H*)-one (3k). White solid, mp 201–203 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.97 (d, J = 7.6 Hz, 2H), 7.79 (d, J = 8.4 Hz, 1H), 7.73–7.69 (m, 1H), 7.61–7.57 (m, 2H), 7.40–7.32 (m, 3H), 7.17–7.09 (m, 3H), 7.01 (d, J = 7.6 Hz, 1H), 6.78–6.75 (m, 3H), 6.55–6.53 (m, 1H), 4.10 (d, J = 10.8 Hz, 1H), 4.06 (d, J = 11.2 Hz, 1H), 2.46 (d, J = 14.8 Hz, 1H), 2.32 (d, J = 14.8 Hz, 1H), 1.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 173.91, 142.22, 142.17, 140.73, 139.49, 137.93, 135.03, 134.48, 133.84, 131.20, 130.82, 128.94, 128.86, 128.65, 128.41, 127.38, 126.50, 124.18, 123.89, 121.80, 121.31, 117.69, 116.80, 86.01, 69.83, 54.59, 43.88, 24.56; IR (KBr, ν, cm^{-1}) 2948, 1716, 1683, 1575, 1496, 1361, 1268, 1173, 861, 760; HRMS (APCI-TOF) *m*/*z* calcd for: $C_{32}H_{25}NO_5SCl$, 570.1142 $[M + H]^+$; found: 570.1139.

5′-((4-Fluorophenyl)sulfonyl)-3*a*′-methyl-1′-phenyl-3′,3*a*′-dihydro-3*H*-spiro[benzo[*b*][1,4]dioxine-2,2′-cyclopenta[*c*]quinolin]-4′(5′*H*)-one (3l). White solid, mp 155–157 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.00–7.97 (m, 2H), 7.74 (d, J = 8.4 Hz, 1H), 7.38–7.34 (m, 4H), 7.29 (s, 1H), 7.25 (d, J = 2.0 Hz, 1H), 7.21–7.19 (m, 2H), 7.11–7.07 (m, 1H), 7.05–7.02 (m, 1H), 6.79–6.72 (m, 3H), 6.57–6.55 (m, 1H), 4.10 (d, J = 10.8 Hz, 1H), 4.05 (d, J = 10.8 Hz, 1H), 2.46 (d, J = 14.8 Hz, 1H), 2.32 (d, J = 14.8 Hz, 1H), 1.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 174.14, 165.78 ($^1J_{CF}$ = 255.50 Hz), 142.26 ($^3J_{CF}$ = 8.30 Hz), 139.94, 139.28, 135.25 ($^4J_{CF}$ = 3.20 Hz), 134.77, 132.63, 131.58, 131.49, 129.35, 128.69, 128.36, 127.46, 126.57, 124.26, 124.24, 121.82, 121.21, 117.68, 116.78, 116.12 ($^2J_{CF}$ = 22.70 Hz), 86.16, 69.90, 54.59, 43.86, 24.62; IR (KBr, ν, cm^{-1}) 2928, 1717, 1683, 1588, 1456, 1369, 1266, 1169, 835, 744; HRMS (APCI-TOF) *m*/*z* calcd for: $C_{32}H_{25}NO_5SF$, 554.1437 $[M + H]^+$; found: 554.1400.

5′-((4-Fluorophenyl)sulfonyl)-1′-(4-methoxyphenyl)-3*a*′-methyl-3′,3*a*′-dihydro-3*H*-spiro[benzo[*b*][1,4]dioxine-2,2′-cyclopenta[*c*]-quinolin]-4′(5′*H*)-one (3m). White solid, mp 160–162 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.00–7.97 (m, 2H), 7.75 (d, J = 8.4 Hz, 1H), 7.38–7.34 (m, 1H), 7.28–7.27 (m, 1H), 7.25–7.23 (m, 1H), 7.15–7.09 (m, 4H), 6.90–6.88 (m, 2H), 6.81–6.77 (m, 3H), 6.58–6.56 (m, 1H), 4.08 (s, 2H), 3.82 (s, 3H), 2.43 (d, J = 14.8 Hz, 1H), 2.32 (d, J = 14.8 Hz, 1H), 1.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 174.26, 165.78 ($^1J_{CF}$ = 255.30 Hz), 159.58, 142.33, 142.27, 139.52, 139.00, 135.28 ($^4J_{CF}$ = 3.10 Hz), 134.80, 131.52 ($^3J_{CF}$ = 9.60 Hz), 130.57, 128.62, 127.54, 126.57, 124.59, 124.52, 124.24, 121.83, 121.22, 117.73, 116.80, 116.13 ($^2J_{CF}$ = 22.70 Hz), 113.89, 86.13, 69.97, 55.27, 54.42, 43.77, 24.52; IR (KBr, ν, cm^{-1}) 3044, 1717, 1693, 1576, 1490, 1387, 1260, 1157, 839, 754; HRMS (APCI-TOF) *m*/*z* calcd for: $C_{33}H_{27}NO_6SF$, 584.1543 $[M + H]^+$; found: 584.1515.

1′-(4-Fluorophenyl)-5′-((4-fluorophenyl)sulfonyl)-3*a*′-methyl-3′,3*a*′-dihydro-3*H*-spiro[benzo[*b*][1,4]dioxine-2,2′-cyclopenta[*c*]-quinolin]-4′(5′*H*)-one (3n). White solid, mp 159–161 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.98–7.95 (m, 2H), 7.74–7.71 (m, 1H), 7.39–7.37 (m, 3H), 7.30–7.27 (m, 2H), 7.18–7.16 (m, 2H), 7.09–7.04 (m, 1H), 6.80–6.76 (m, 3H), 6.75–6.72 (m, 1H), 6.56–6.54 (m, 1H), 4.08 (d, J = 10.8 Hz, 1H), 4.02 (d, J = 10.8 Hz, 1H), 2.46 (d, J = 15.2 Hz, 1H), 2.31 (d, J = 14.8 Hz, 1H), 1.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 173.76, 160.42 ($^1J_{CF}$ = 247.00 Hz), 142.26, 142.09, 140.69, 139.06, 134.97 ($^5J_{CF}$ = 3.20 Hz), 132.07, 131.59 ($^3J_{CF}$ = 9.70 Hz), 129.10, 128.70, 128.54, 126.15 ($^4J_{CF}$ = 8.80 Hz), 121.88, 121.31, 117.63, 116.83, 116.29, 116.06, 115.68 ($^2J_{CF}$ = 23.10 Hz), 114.35, 114.10, 86.10, 69.78, 54.51, 43.84, 24.55; IR (KBr, ν, cm^{-1}) 2926, 1716, 1683, 1540, 1495, 1374, 1262, 1179, 836, 747; HRMS (APCI-TOF) *m*/*z* calcd for: $C_{32}H_{24}NO_5SF_2$, 572.1343 $[M + H]^+$; found: 572.1318.

5′-((4-Chlorophenyl)sulfonyl)-3*a*′-methyl-1′-phenyl-3′,3*a*′-dihydro-3*H*-spiro[benzo[*b*][1,4]dioxine-2,2′-cyclopenta[*c*]quinolin]-4′(5′*H*)-one (3o). White solid, mp 200–201 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.90 (d, J = 8.8 Hz, 2H), 7.74 (d, J = 8.4 Hz, 1H), 7.58–7.56 (m, 2H), 7.40–7.35 (m, 4H), 7.22–7.19 (m, 2H),

7.12–7.08 (m, 1H), 7.06–7.04 (m, 1H), 6.82–6.77 (m, 3H), 6.60–6.58 (m, 1H), 4.11 (d, J = 10.8 Hz, 1H), 4.04 (d, J = 10.4 Hz, 1H), 2.50 (d, J = 14.8 Hz, 1H), 2.30 (d, J = 14.8 Hz, 1H), 1.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 174.05, 142.31, 142.20, 140.54, 139.98, 139.40, 137.82, 134.69, 132.61, 130.03, 129.36, 129.14, 128.72, 128.39, 127.48, 126.64, 124.29, 124.23, 121.86, 121.24, 117.86, 116.77, 86.19, 69.92, 54.62, 43.76, 24.60; IR (KBr, ν, cm^{-1}) 2976, 1716, 1668, 1538, 1417, 1368, 1265, 1122, 885, 754; HRMS (APCI-TOF) m/z calcd for: $C_{32}H_{25}NO_5SCl$, 570.1142 $[M + H]^+$; found: 570.1158.

5′-((4-Chlorophenyl)sulfonyl)-3*a*′-methyl-1′-(*p*-tolyl)-3′,3*a*′-dihydro -3*H*-spiro[benzo[*b*][1,4]dioxine-2,2′-cyclopenta[*c*]quinolin]-4′(5′*H*)-one (3p). White solid, mp 189–191 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.89–7.87 (m, 2H), 7.74 (d, J = 8.4 Hz, 1H), 7.57–7.54 (m, 2H), 7.38–7.34 (m, 1H), 7.17 (d, J = 8.0 Hz, 2H), 7.11–7.08 (m, 4H), 6.79–6.78 (m, 3H), 6.59–6.57 (m, 1H), 4.09 (d, J = 11.2 Hz, 1H), 4.03 (d, J = 10.8 Hz, 1H), 2.47 (d, J = 14.8 Hz, 1H), 2.36 (s, 3H), 2.29 (d, J = 14.8 Hz, 1H), 1.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 174.10, 142.33, 142.21, 140.50, 139.67, 139.40, 138.25, 137.84, 134.74, 134.68, 129.99, 129.49, 129.19, 129.11, 128.61, 127.52, 126.62, 124.49, 124.22, 121.81, 121.19, 117.90, 116.74, 86.18, 69.96, 54.54, 43.68, 30.94, 24.52, 21.28; IR (KBr, ν, cm^{-1}) 2924, 1716, 1683, 1583, 1490, 1371, 1260, 1167, 835, 757; HRMS (APCI-TOF) m/z calcd for: $C_{33}H_{27}NO_5SCl$, 584.1298 $[M + H]^+$; found: 584.1266.

5′-((4-Chlorophenyl)sulfonyl)-1′-(4-methoxyphenyl)-3*a*′-methyl-3′,3*a*′-dihydro-3*H*-spiro[benzo[*b*][1,4]dioxine-2,2′-cyclopenta[*c*]-quinolin]-4′(5′*H*)-one (3q). White solid, mp 198–200 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.88 (d, J = 8.8 Hz, 2H), 7.74 (d, J = 8.0 Hz, 1H), 7.55 (d, J = 8.8 Hz, 2H), 7.38–7.34 (m, 1H), 7.15–7.08 (m, 4H), 6.89 (d, J = 8.8 Hz, 2H), 6.80–6.77 (m, 3H), 6.60–6.57 (m, 1H), 4.09 (d, J = 10.8 Hz, 1H), 4.05 (d, J = 11.2 Hz, 1H), 3.82 (s, 3H), 2.46 (d, J = 14.8 Hz, 1H), 2.29 (d, J = 14.8 Hz, 1H), 1.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 174.14, 159.58, 142.32, 142.23, 140.51, 139.58, 139.11, 137.83, 134.69, 130.56, 129.99, 129.12, 128.61, 127.54, 126.62, 124.56, 124.54, 124.21, 121.84, 121.22, 117.88, 116.76, 113.89, 86.15, 69.98, 55.28, 54.43, 43.66, 24.49; IR (KBr, ν, cm^{-1}) 3056, 1717, 1684, 1559, 1436, 1373, 1260, 1175, 837, 751; HRMS (APCI-TOF) m/z calcd for: $C_{33}H_{27}NO_6SCl$, 600.1248 $[M + H]^+$; found: 600.1212.

1′-(4-Chlorophenyl)-5′-((4-chlorophenyl)sulfonyl)-3*a*′-methyl-3′,3*a*′-dihydro-3*H*-spiro[benzo[*b*][1,4]dioxine-2,2′-cyclopenta[*c*]-quinolin]-4′(5′*H*)-one (3r). White solid, mp 214–216 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.91–7.89 (m, 2H), 7.75 (d, J = 8.0 Hz, 1H), 7.57–7.55 (m, 2H), 7.41–7.33 (m, 3H), 7.15–7.11 (m, 3H), 7.03–7.01 (m, 1H), 6.82–6.77 (m, 3H), 6.60–6.57 (m, 1H), 4.09 (d, J = 10.8 Hz, 1H), 4.03 (d, J = 10.8 Hz, 1H), 2.50 (d, J = 14.8 Hz, 1H), 2.30 (d, J = 14.8 Hz, 1H), 1.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 173.87, 142.20, 140.64, 138.13, 137.74, 134.71, 134.57, 131.06, 130.75, 130.03, 129.14, 128.98, 128.70, 127.40, 126.69, 124.22, 123.95, 121.96, 121.39, 117.77, 116.81, 86.10, 69.83, 54.64, 43.80, 24.56; IR (KBr, ν, cm^{-1}) 2976, 1716, 1699, 1591, 1491, 1365, 1259, 1183, 833, 771; HRMS (APCI-TOF) m/z calcd for: $C_{32}H_{24}NO_5SCl_2$, 604.0752 $[M + H]^+$; found: 604.0749.

5′-((4-Bromophenyl)sulfonyl)-3*a*′-methyl-1′-phenyl-3′,3*a*′-dihydro-3*H*-spiro[*b*enzo[*b*][1,4]dioxine-2,2′-cyclopenta[*c*]quinolin]-4′(5′*H*)-one (3s). White solid, mp 205–206 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.83–7.80 (m, 2H), 7.75–7.72 (m, 3H), 7.39–7.34 (m, 4H), 7.21–7.19 (m, 2H), 7.12–7.08 (m, 1H), 7.06–7.04 (m, 1H), 6.82–6.76 (m, 3H), 6.60 (d, J = 7.6 Hz, 1H), 4.11 (d, J = 10.8 Hz, 1H), 4.03 (d, J = 11.2 Hz, 1H), 2.51 (d, J = 14.0 Hz, 1H), 2.29 (d, J = 14.8 Hz, 1H), 1.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 174.00, 142.31, 142.19, 140.00, 139.43, 138.41, 134.66, 132.62, 132.13, 130.06, 129.36, 129.18, 128.72, 128.39, 127.48, 126.65, 124.31, 124.22, 121.88, 121.25, 117.98, 116.77, 86.19, 69.94, 54.62, 43.73, 24.59; IR (KBr, ν, cm^{-1}) 2977, 1718, 1652, 1570, 1491, 1367, 1264, 1168, 832, 756; HRMS (APCI-TOF) m/z calcd for: $C_{32}H_{25}NO_5SBr$, 614.0637 $[M + H]^+$; found: 614.0610.

1′-(4-Chlorophenyl)-5′-((4-chlorophenyl)sulfonyl)-3*a*′-methyl-3′,3*a*′-dihydro-3*H*-spiro[benzo[*b*][1,4]dioxine-2,2′-cyclopenta[*c*]-quinolin]-4′(5′*H*)-one (3t). White solid, mp 216–217 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.81–7.78 (m, 2H), 7.75–7.71 (m, 3H), 7.38–7.34 (m, 1H), 7.15–7.10 (m, 4H), 6.90–6.88 (m, 2H), 6.81–6.77 (m, 3H), 6.60 (d, J = 6.8 Hz, 1H), 4.09 (d, J = 10.8 Hz, 1H), 4.05 (d, J = 10.8 Hz, 1H), 3.82 (s, 3H), 2.47 (d, J = 14.8 Hz, 1H), 2.28 (d, J = 15.2 Hz, 1H), 1.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 174.08, 159.59, 142.32, 142.21, 139.59, 139.13, 138.42, 134.66, 132.09, 130.56, 130.01, 129.12, 128.60, 127.53, 126.62, 124.55, 124.18, 121.84, 121.21, 117.98, 116.74, 113.88, 86.15, 69.98, 55.26, 54.43, 43.62, 24.46; IR (KBr, ν, cm^{-1}) 2926, 1717, 1683, 1575, 1490, 1368, 1247, 1168, 838, 748; HRMS (APCI-TOF) m/z calcd for: $C_{33}H_{28}NO_6SBr$, 644.0742 $[M + H]^+$; found: 644.0704.

3*a*′-Methyl-5′-(naphthalen-1-ylsulfonyl)-1′-phenyl-3′,3*a*′-dihydro-3*H*-spiro[benzo[*b*][1,4]dioxine-2,2′-cyclopenta[*c*]quinolin]-4′(5′*H*)-one (3u). White solid, mp 210–211 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.59 (d, J = 1.6 Hz, 1H), 8.05–7.99 (m, 3H), 7.85–7.82 (m, 2H), 7.76–7.66 (m, 2H), 7.41–7.35 (m, 4H), 7.20–7.18 (m, 2H), 7.13–7.09 (m, 1H), 7.06–7.04 (m, 1H), 6.70–6.63 (m, 2H), 6.52–6.48 (m, 1H), 5.70–5.68 (m, 1H), 4.05 (d, J = 10.8 Hz, 1H), 3.95 (d, J = 10.4 Hz, 1H), 2.44–2.40 (m, 1H), 2.19 (d, J = 14.8 Hz, 1H), 1.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 142.19, 142.00, 140.36, 139.16, 136.09, 135.40, 134.95, 132.72, 131.84, 130.93, 129.81, 129.50, 129.41, 129.01, 128.64, 128.29, 127.94, 127.71, 127.36, 126.48, 124.44, 124.37, 122.80, 121.45, 120.98, 117.58, 116.53, 86.04, 69.90, 54.61, 43.56, 24.53; IR (KBr, ν, cm^{-1}) 2924, 1716, 1683, 1558, 1495, 1362, 1263, 1170, 752, 669; HRMS (APCI-TOF) m/z calcd for: $C_{36}H_{28}NO_5S$, 586.1688 $[M + H]^+$; found: 586.1662.

1′-(4-Methoxyphenyl)-3*a*′-methyl-5′-(naphthalen-1-ylsulfonyl)-3′,3*a*′-dihydro-3*H*-spiro[benzo[*b*][1,4]dioxine-2,2′-cyclopenta[*c*]-quinolin]-4′(5′*H*)-one (3v). White solid, mp 174–176 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.59 (d, J = 1.2 Hz, 1H), 8.04–7.98 (m, 3H), 7.85–7.81 (m, 2H), 7.75–7.72 (m, 1H), 7.69–7.65 (m, 1H), 7.41–7.37 (m, 1H), 7.15–7.08 (m, 4H), 6.90–6.87 (m, 2H), 6.72–6.64 (m, 2H), 6.53–6.49 (m, 1H), 5.74–5.71 (m, 1H), 4.04 (d, J = 11.2 Hz, 1H), 3.98 (d, J = 10.8 Hz, 1H), 3.83 (s, 3H), 2.39 (d, J = 14.8 Hz, 1H), 2.18 (d, J = 14.8 Hz, 1H), 1.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 173.95, 159.53, 142.22, 142.05, 139.99, 138.88, 136.12, 135.39, 134.97, 131.84, 130.89, 130.62, 129.80, 129.47, 129.01, 128.55, 127.93, 127.69, 127.44, 126.47, 124.70, 124.35, 122.75, 121.45, 120.97, 117.62, 116.53, 113.81, 86.02, 69.96, 55.27, 54.43, 43.48, 24.43; IR (KBr, ν, cm^{-1}) 2927, 1716, 1653, 1594, 1494, 1361, 1264, 1173, 834, 772; HRMS (APCI-

TOF) *m*/*z* calcd for: $C_{37}H_{30}NO_6S$, 616.1794 $[M + H]^+$; found: 616.1761.

5′-((4-Bromophenyl)sulfonyl)-8′-fluoro-3*a*′-methyl-1′-(*p*-tolyl)-3′,3*a*′-dihydro-3*H*-spiro[benzo[*b*][1,4]dioxine-2,2′-cyclopenta[*c*]quinolin]-4′(5′*H*)-one (3w). White solid, mp 225–227 °C; ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm) 7.79–7.69 (m, 5H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.09–7.04 (m, 3H), 6.81–6.78 (m, 4H), 6.59 (d, *J* = 7.2 Hz, 1H), 4.07 (d, *J* = 10.8 Hz, 1H), 3.99 (d, *J* = 11.2 Hz, 1H), 2.48 (d, *J* = 14.8 Hz, 1H), 2.37 (s, 3H), 2.27 (d, *J* = 14.8 Hz, 1H), 1.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; *δ*, ppm) 173.66, 166.45 ($^1J_{CF}$ = 246.80 Hz), 142.29, 141.07, 140.83, 138.79, 138.63, 138.09, 132.15, 130.69 ($^6J_{CF}$ = 3.2 Hz), 130.03, 129.28, 128.95, 128.90, 126.46 ($^4J_{CF}$ = 8.80 Hz), 126.09 ($^5J_{CF}$ = 8.5 Hz), 121.88, 121.27, 117.96, 116.77, 115.58 ($^2J_{CF}$ = 22.9 Hz), 114.31 ($^2J_{CF}$ = 24.3 Hz), 99.98, 86.12, 69.83, 54.47, 43.60, 24.41, 21.29; IR (KBr, *ν*, cm^{-1}) 2973, 1717, 1652, 1591, 1491, 1373, 1254, 1173, 868, 744; HRMS (APCI-TOF) *m*/*z* calcd for: $C_{33}H_{26}NO_5SBrF$, 646.0699 $[M + H]^+$; found: 646.0701.

8′-Chloro-3*a*′-methyl-1′-phenyl-5′-tosyl-3′,3*a*′-dihydro-3*H*-spiro[benzo[*b*][1,4]dioxine-2,2′-cyclopenta[*c*]quinolin]-4′(5′*H*)-one (3x). White solid, mp 230–232 °C; ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm) 7.83 (d, *J* = 8.4 Hz, 2H), 7.71 (d, *J* = 8.8 Hz, 1H), 7.40–7.37 (m, 5H), 7.33–7.30 (m, 1H), 7.20–7.18 (m, 2H), 6.98 (d, *J* = 2.4 Hz, 1H), 6.78–6.74 (m, 3H), 6.51–6.48 (m, 1H), 4.10 (d, *J* = 10.8 Hz, 1H), 4.05 (d, *J* = 11.6 Hz, 1H), 2.51 (s, 3H), 2.46 (d, *J* = 14.8 Hz, 1H), 2.30 (d, *J* = 14.8 Hz, 1H), 1.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; *δ*, ppm) 173.59, 145.10, 142.30, 142.17, 140.49, 138.99, 136.23, 133.50, 132.12, 132.01, 129.52, 129.20, 128.66, 128.63, 128.57, 128.49, 127.14, 125.79, 125.39, 121.66, 121.27, 117.63, 116.85, 86.05, 69.78, 54.41, 43.80, 24.53, 21.79; IR (KBr, *ν*, cm^{-1}) 2970, 1717, 1683, 1594, 1493, 1373, 1284, 1174, 878, 749; HRMS (APCI-TOF) *m*/*z* calcd for: $C_{33}H_{27}NO_5SCl$, 584.1298 $[M + H]^+$; found: 584.1279.

8′-Chloro-3*a*′-methyl-1′-(*p*-tolyl)-5′-tosyl-3′,3*a*′-dihydro-3*H*-spiro[benzo[*b*][1,4]dioxine-2,2′-cyclopenta[*c*]quinolin]-4′(5′*H*)-one (3y). White solid, mp 224–226 °C; ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm) 7.82 (d, *J* = 8.4 Hz, 2H), 7.71 (d, *J* = 8.8 Hz, 1H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.33–7.30 (m, 1H), 7.19 (d, *J* = 7.6 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 7.03 (d, *J* = 2.4 Hz, 1H), 6.78–6.75 (m, 3H), 6.50–6.48 (m, 1H), 4.07 (d, *J* = 10.8 Hz, 1H), 4.04 (d, *J* = 11.6 Hz, 1H), 2.51 (s, 3H), 2.44 (d, *J* = 14.8 Hz, 1H), 2.37 (s, 3H), 2.29 (d, *J* = 14.8 Hz, 1H), 1.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; *δ*, ppm) 173.64, 145.06, 142.34, 142.20, 140.49, 138.65, 138.54, 136.24, 133.51, 132.00, 129.51, 129.22, 129.05, 128.97, 128.55, 127.18, 126.03, 125.42, 121.64, 121.23, 117.68, 116.83, 86.05, 69.82, 54.36, 43.68, 24.42, 21.78, 21.32; IR (KBr, *ν*, cm^{-1}) 2970, 1721, 1646, 1595, 1492, 1307, 1286, 1174, 810, 761; HRMS (APCI-TOF) *m*/*z* calcd for: $C_{34}H_{29}NO_5SCl$, 598.1455 $[M + H]^+$; found: 598.1429.

1′,3*a*′-Diphenyl-5′-tosyl-3′,3*a*′-dihydro-3*H*-spiro[benzo[*b*][1,4]dioxine-2,2′-cyclopenta[*c*]quinolin]-4′(5′*H*)-one (3z). White solid, mp 214–215 °C; ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm) 7.87 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 1H), 7.42–7.38 (m, 5H), 7.34–7.32 (m, 2H), 7.22–7.10 (m, 7H), 7.05–7.01 (m, 1H), 6.78–6.69 (m, 3H), 6.55–6.52 (m, 1H), 4.05 (d, *J* = 10.8 Hz, 1H), 3.91 (d, *J* = 10.8 Hz, 1H), 2.80 (d, *J* = 14.4 Hz, 1H), 2.56–2.47 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$; *δ*, ppm) 171.71, 144.89, 142.67, 142.35, 142.27, 139.32, 137.43, 136.63, 134.78, 132.76, 129.46, 128.96, 128.54, 128.52, 128.45, 127.69, 127.23, 126.41, 126.02, 125.36, 124.44, 121.60, 121.19, 117.58, 116.79, 86.24, 69.12, 62.69, 47.20, 21.79; IR (KBr, *ν*, cm^{-1}) 2922, 1725, 1646, 1541, 1457, 1360, 1266, 1168, 944, 759; HRMS (APCI-TOF) *m*/*z* calcd for: $C_{38}H_{30}NO_5S$, 612.1845 $[M + H]^+$; found: 612.1838.

3*a*′,5′-Dimethyl-1′-phenyl-3′,3*a*′-dihydro-3*H*-spiro[benzo[*b*][1,4]dioxine-2,2′-cyclopenta[*c*]quinolin]-4′(5′*H*)-one (3aa). White solid, mp 197–198 °C; ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm) 7.36–7.31 (m, 3H), 7.29–7.28 (m, 1H), 7.26–7.24 (m, 2H), 7.04 (d, *J* = 8.0 Hz, 1H), 6.97 (d, *J* = 7.6 Hz, 1H), 6.84–6.76 (m, 5H), 4.23 (d, *J* = 11.2 Hz, 1H), 4.20 (d, *J* = 12.0 Hz, 1H), 3.42 (s, 3H), 2.81 (d, *J* = 14.4 Hz, 1H), 2.63 (d, *J* = 14.8 Hz, 1H), 1.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; *δ*, ppm) 174.02, 142.66, 142.48, 141.23, 140.10, 137.76, 133.86, 129.74, 129.49, 128.29, 127.90, 127.69, 122.52, 121.64, 120.99, 120.18, 117.92, 116.67, 115.00, 85.86, 70.13, 51.49, 44.06, 30.06, 26.86; IR (KBr, *ν*, cm^{-1}) 2969, 1772, 1637, 1540, 1452, 1376, 1252, 1186, 941, 754; HRMS (APCI-TOF) *m*/*z* calcd for: $C_{27}H_{24}NO_3$, 410.1756 $[M + H]^+$; found: 410.1763.

1′-(4-Chlorophenyl)-3*a*′,5′-dimethyl-3′,3*a*′-dihydro-3*H*-spiro-[benzo[*b*][1,4]dioxine-2,2′-cyclopenta[*c*]quinolin]-4′(5′*H*)-one (3bb). White solid, mp 193–194 °C; ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm) 7.32–7.26 (m, 3H), 7.19 (d, *J* = 8.4 Hz, 2H), 7.06 (d, *J* = 8.4 Hz, 1H), 6.96 (d, *J* = 7.6 Hz, 1H), 6.85–6.81 (m, 2H), 6.79–6.75 (m, 3H), 4.22 (d, *J* = 10.8 Hz, 1H), 4.18 (d, *J* = 11.2 Hz, 1H), 3.42 (s, 3H), 2.80 (d, *J* = 15.2 Hz, 1H), 2.61 (d, *J* = 14.8 Hz, 1H), 1.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; *δ*, ppm) 173.84, 142.54, 142.40, 141.96, 140.13, 136.50, 134.02, 132.36, 131.19, 129.76, 128.60, 127.65, 122.63, 121.76, 121.14, 119.84, 117.81, 116.73, 115.13, 85.78, 70.10, 51.54, 44.13, 30.07, 26.79; IR (KBr, *ν*, cm^{-1}) 2973, 1717, 1617, 1541, 1458, 1385, 1274, 1147, 938, 763; HRMS (APCI-TOF) *m*/*z* calcd for: $C_{27}H_{23}NO_3Cl$, 444.1366 $[M + H]^+$; found: 444.1352.

5-((4-Chlorophenyl)sulfonyl)-3*a*-methyl-1-phenyl-3,3*a*-dihydro spiro[cyclopenta[*c*]quinoline-2,1′-cyclopentan]-4(5*H*)-one (5a). White solid, mp 149–151 °C; ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm) 7.91 (d, *J* = 8.4 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.38–7.34 (m, 3H), 7.23 (d, *J* = 8.0 Hz, 1H), 7.08–7.06 (m, 2H), 7.00–6.96 (m, 1H), 6.78 (d, *J* = 7.6 Hz, 1H), 2.20 (d, *J* = 13.6 Hz, 1H), 1.87 (d, *J* = 13.6 Hz, 1H), 1.84–1.81 (m, 1H), 1.63–1.56 (m, 3H), 1.53–1.47 (m, 1H), 1.43–1.39 (m, 1H), 1.32–1.24 (m, 1H), 1.17 (s, 3H), 0.87–0.82 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$; *δ*, ppm) 176.22, 147.60, 140.36, 138.17, 135.40, 134.49, 132.44, 129.98, 129.28, 128.91, 128.30, 127.58, 127.39, 127.26, 126.32, 125.82, 123.88, 59.44, 55.08, 48.61, 38.35, 38.15, 24.60, 24.26, 23.62; IR (KBr, *ν*, cm^{-1}) 2961, 1718, 1595, 1496, 1396, 1282, 1181, 1099, 827, 773; HRMS (APCI-TOF) *m*/*z* calcd for: $C_{29}H_{27}NO_3SCl$, 504.1400 $[M + H]^+$; found: 504.1395.

3*a*,5-Dimethyl-1-phenyl-3,3*a*-dihydrospiro[cyclopenta[*c*]quinoline-2,1′-cyclopentan]-4(5*H*)-one (5b). White solid, mp 152–154 °C; ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm) 7.36–7.31 (m, 3H), 7.17–7.13 (m, 3H), 6.98 (d, *J* = 8.4 Hz, 1H), 6.76 (d, *J* = 6.8 Hz, 1H), 6.71–6.68 (m, 1H), 3.40 (s, 3H), 2.45 (d, *J* = 13.2 Hz, 1H), 2.15 (d, *J* = 13.2 Hz, 1H), 1.96–1.87 (m, 1H), 1.81–1.72 (m, 2H), 1.72–1.58 (m, 2H), 1.53–1.37 (m, 2H), 1.34 (s, 3H), 1.32–1.19 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$; *δ*, ppm) 175.84, 146.04, 139.77, 136.89, 133.96, 129.43, 128.30, 127.92, 127.44, 127.11, 122.23,

121.63, 114.74, 58.80, 52.04, 48.86, 39.00, 38.44, 29.94, 26.53, 24.25, 23.96; IR (KBr, ν, cm^{-1}) 2955, 1684, 1597, 1472, 1374, 1289, 1162, 1098, 838, 785; HRMS (APCI-TOF) *m*/*z* calcd for: $C_{24}H_{26}NO$, 344.2014 $[M + H]^+$; found: 334.2019.

5′-((4-Chlorophenyl)sulfonyl)-3*a*′-methyl-1′-phenyl-3′,3*a*′-dihydro spiro[cyclohexane-1,2′-cyclopenta[*c*]quinolin]-4′(5′*H*)-one (5c). White solid, mp 195–197 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.91 (d, J = 8.4 Hz, 2H), 7.67 (d, J = 8.4 Hz, 1H), 7.49 (d, J = 8.4 Hz, 2H), 7.38–7.36 (m, 3H), 7.23 (d, J = 8.0 Hz, 1H), 7.02–6.96 (m, 3H), 6.72 (d, J = 7.6 Hz, 1H), 2.36 (d, J = 14.0 Hz, 1H), 1.89 (d, J = 14.0 Hz, 1H), 1.64–1.60 (m, 1H), 1.56–1.51 (m, 3H), 1.43–1.34 (m, 2H), 1.26–1.22 (m, 1H), 1.15 (s, 3H), 1.02–0.95 (m, 1H), 0.92–0.84 (m, 1H), 0.50 (d, J = 12.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 176.03, 150.35, 140.36, 137.98, 135.36, 134.41, 131.68, 130.15, 129.31, 128.83, 128.16, 127.51, 127.32, 127.18, 126.32, 126.03, 123.96, 54.89, 52.93, 43.51, 36.19, 36.14, 25.23, 25.13, 23.06, 22.36; IR (KBr, ν, cm^{-1}) 2966, 1717, 1595, 1494, 1396, 1294, 1181, 1020, 828, 793; HRMS (APCI-TOF) *m*/*z* calcd for: $C_{30}H_{29}NO_3SCl$, 518.1557 $[M + H]^+$; found: 518.1555.

3*a*′,5′-Dimethyl-1′-phenyl-3′,3*a*′-dihydrospiro[cyclohexane-1,2′-cyclopenta[*c*]quinolin]-4′(5′*H*)-one (5d). White solid, mp 148–150 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.36–7.32 (m, 3H), 7.16–7.09 (m, 3H), 6.98 (d, J = 8.0 Hz, 1H), 6.69 (d, J = 4.4 Hz, 2H), 3.40 (s, 3H), 2.46 (d, J = 14.0 Hz, 1H), 2.29 (d, J = 14.0 Hz, 1H), 1.72–1.67 (m, 3H), 1.61–1.55 (m, 2H), 1.54–1.50 (m, 1H), 1.41–1.39 (m, 1H), 1.32 (s, 3H), 1.16–1.09 (m, 1H), 0.98–0.94 (m, 1H), 0.89–0.84 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 176.01, 148.80, 139.81, 136.87, 133.20, 129.53, 128.23, 127.91, 127.55, 127.10, 122.26, 121.83, 114.73, 52.21, 51.89, 43.56, 37.64, 35.87, 30.00, 27.33, 25.42, 23.50, 22.38; IR (KBr, ν, cm^{-1}) 2922, 1674, 1598, 1459, 1368, 1268, 1105, 1047, 914, 773; HRMS (APCI-TOF) *m*/*z* calcd for: $C_{25}H_{28}NO$, 358.2171 $[M + H]^+$; found: 358.2174.

5′-((4-Chlorophenyl)sulfonyl)-3*a*′,4-dimethyl-1′-phenyl-3′,3*a*′-dihydrospiro[cyclohexane-1,2′-cyclopenta[*c*]quinolin]-4′(5′*H*)-one (5e, major). White solid, mp 168–170 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.90 (d, J = 8.4 Hz, 2H), 7.66 (d, J = 8.0 Hz, 1H), 7.49 (d, J = 8.4 Hz, 2H), 7.38–7.35 (m, 4H), 7.06–7.02 (m, 3H), 6.71 (d, J = 7.6 Hz, 1H), 2.32 (d, J = 14.0 Hz, 1H), 1.91 (d, J = 14.0 Hz, 1H), 1.65–1.51 (m, 4H), 1.37–1.24 (m, 4H), 1.15 (s, 3H), 0.81 (d, J = 5.2 Hz, 1H), 0.71 (d, J = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 176.10, 150.42, 140.36, 137.98, 135.52, 134.42, 131.71, 131.15, 130.13, 129.30, 128.84, 128.23, 127.51, 127.38, 127.18, 126.32, 126.02, 123.95, 54.80, 53.02, 43.68, 36.11, 28.45, 27.74, 25.87, 25.20, 17.07. IR (KBr, ν, cm^{-1}) 2958, 1717, 1593, 1488, 1372, 1263, 1132, 1042, 858, 773; HRMS (APCI-TOF) *m*/*z* calcd for: $C_{31}H_{31}NO_3SCl$, 532.1713 $[M + H]^+$; found: 532.1717.

5′-((4-Chlorophenyl)sulfonyl)-3*a*′-methyl-1′-phenyl-3′,3*a*′-dihydro spiro[cyclobutane-1,2′-cyclopenta[*c*]quinolin]-4′(5′*H*)-one (5f). White solid, mp 149–151 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.92 (d, J = 8.8 Hz, 2H), 7.65 (d, J = 8.0 Hz, 1H), 7.49 (d, J = 8.4 Hz, 2H), 7.44–7.38 (m, 3H), 7.24–7.19 (m, 3H), 7.00–6.96 (m, 1H), 6.82 (d, J = 7.6 Hz, 1H), 2.51–2.44 (m, 1H), 2.35 (d, J = 13.6 Hz, 1H), 2.29 (d, J = 13.6 Hz, 1H), 2.12–2.05 (m, 1H), 1.96–1.80 (m, 2H), 1.55–1.50 (m, 2H), 1.14 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 176.16, 146.85, 140.35, 138.24, 135.64, 134.72, 132.42, 129.92, 128.96, 128.85, 128.55, 127.75, 127.47, 127.41, 126.24, 125.40, 123.72, 55.08, 54.55, 49.83, 34.32, 31.93, 23.94, 16.52; IR (KBr, ν, cm^{-1}) 2948, 1721, 1599, 1476, 1371, 1284, 1182, 1114, 827, 795; HRMS (APCI-TOF) *m*/*z* calcd for: $C_{28}H_{26}NO_3SCl$, 490.1244 $[M + H]^+$; found: 490.1241.

3*a*′,5′-Dimethyl-1′-phenyl-3′,3*a*′-dihydrospiro[cyclobutane-1,2′-cyclopenta[*c*]quinolin]-4′(5′*H*)-one (5g). White solid, mp 158–160 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.42–7.34 (m, 3H), 7.24 (d, J = 7.2 Hz, 2H), 7.17–7.13 (m, 1H), 6.98 (d, J = 8.0 Hz, 1H), 6.81 (d, J = 7.6 Hz, 1H), 6.72–6.69 (m, 1H), 3.39 (s, 3H), 2.60 (d, J = 13.2 Hz, 1H), 2.55 (d, J = 8.0 Hz, 1H), 2.53–2.47 (m, 1H), 2.25–2.18 (m, 1H), 2.11–2.04 (m, 1H), 1.96–1.89 (m, 1H), 1.82–1.75 (m, 1H), 1.59–1.51 (m, 1H), 1.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 175.49, 145.50, 139.96, 137.10, 134.01, 129.00, 128.53, 128.08, 127.41, 127.25, 122.24, 121.28, 114.81, 54.15, 51.96, 50.20, 35.05, 31.89, 29.84, 25.77, 16.72; IR (KBr, ν, cm^{-1}) 2969, 1668, 1595, 1459, 1369, 1284, 1117, 1097, 920, 758; HRMS (APCI-TOF) *m*/*z* calcd for: $C_{23}H_{24}NO$, 330.1858 $[M + H]^+$; found: 330.1860.

5-((4-Chlorophenyl)sulfonyl)-2,2-diethyl-3*a*-methyl-1-phenyl-3,3*a*-dihydro-2*H*-cyclopenta[*c*]quinolin-4(5*H*)-onen (5h). White solid, mp 149–151 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.93 (d, J = 8.8 Hz, 2H), 7.75 (d, J = 8.0 Hz, 1H), 7.46 (d, J = 8.4 Hz, 2H), 7.33–7.32 (m, 3H), 7.27–7.23 (m, 1H), 7.05–7.03 (m, 2H), 7.00–6.96 (m, 1H), 6.70–6.68 (m, 1H), 2.45 (d, J = 14.8 Hz, 1H), 1.67 (d, J = 14.8 Hz, 1H), 1.63–1.60 (m, 1H), 1.55–1.50 (m, 1H), 1.13 (s, 3H), 1.10–1.06 (m, 1H), 1.02–0.99 (m, 3H), 0.94–0.87 (m, 1H), 0.16–0.12 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 175.33, 145.79, 140.43, 137.93, 135.36, 134.66, 134.36, 130.53, 129.05, 128.80, 128.38, 127.63, 127.58, 127.22, 126.22, 126.09, 123.91, 57.54, 54.76, 39.82, 31.94, 31.28, 24.50, 9.92, 8.11; IR (KBr, ν, cm^{-1}) 2970, 1719, 1584, 1478, 1374, 1297, 1186, 1091, 835, 790; HRMS (APCI-TOF) *m*/*z* calcd for: $C_{29}H_{29}NO_3SCl$, 506.1557 $[M + H]^+$; found: 506.1555.

2,2-Diethyl-3*a*,5-dimethyl-1-phenyl-3,3*a*-dihydro-2*H*-cyclopenta[*c*]quinolin-4(5*H*)-one (5i). White solid, mp 153–155 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.31–7.28 (m, 3H), 7.18–7.14 (m, 1H), 7.10–7.08 (m, 2H), 6.99 (d, J = 8.0 Hz, 1H), 6.73–6.65 (m, 2H), 3.42 (s, 3H), 2.73 (d, J = 14.8 Hz, 1H), 1.87 (d, J = 14.8 Hz, 1H), 1.67–1.62 (m, 2H), 1.34–1.29 (m, 1H), 1.27 (s, 3H), 1.23–1.16 (m, 1H), 1.10–1.06 (m, 3H), 0.75–0.72 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 175.74, 145.25, 139.75, 136.55, 135.48, 129.28, 128.21, 127.78, 127.65, 127.07, 122.33, 122.10, 114.58, 56.73, 52.01, 39.90, 31.44, 31.39, 30.14, 26.40, 10.22, 8.74, 1.04; IR (KBr, ν, cm^{-1}) 2940, 1670, 1589, 1464, 1379, 1270, 1135, 1047, 870, 775; HRMS (APCI-TOF) *m*/*z* calcd for: $C_{24}H_{28}NO$, 346.2171 $[M + H]^+$; found: 346.2172.

5-((4-Chlorophenyl)sulfonyl)-2,2,3*a*-trimethyl-1-phenyl-3,3*a*-dihydro-2*H*-cyclopenta[*c*]quinolin-4(5*H*)-one (5j). White solid, mp 157–160 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.91 (d, J = 8.4 Hz, 2H), 7.68 (d, J = 8.0 Hz, 1H), 7.50 (d, J = 8.4 Hz, 2H), 7.38–7.34 (m, 3H), 7.25–7.23 (m, 1H), 7.08–7.05 (m, 2H), 7.01–7.00 (m, 1H), 6.77 (d, J = 7.6 Hz, 1H), 2.29 (d, J = 13.6 Hz, 1H), 1.86 (d, J = 14.0 Hz, 1H), 1.28 (s, 3H), 1.17 (s, 3H), 0.67 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 176.02, 149.72, 140.36, 138.14, 135.31, 134.61, 131.38, 130.69, 130.00, 128.91, 128.89, 128.33, 127.76, 127.63, 127.42, 127.32, 126.35, 123.97, 54.80, 49.24, 48.53, 29.16, 28.59, 24.55; IR (KBr, ν, cm^{-1}) 2954, 1717, 1583, 1478, 1397, 1298, 1186, 1092, 833, 759; HRMS (APCI-TOF)

m/*z* calcd for: $C_{27}H_{25}NO_3SCl$, 478.1244 $[M + H]^+$; found: 478.1243.

2,2,3*a*,5-Tetramethyl-1-phenyl-3,3*a*-dihydro-2*H*-cyclopenta[*c*]-quinolin-4(5*H*)-one (5k). White solid, mp 147–149 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.34–7.31 (m, 3H), 7.18–7.12 (m, 4H), 6.74–6.70 (m, 2H), 3.40 (s, 3H), 2.57 (d, J = 13.6 Hz, 1H), 2.08 (d, J = 13.6 Hz, 1H), 1.39 (s, 3H), 1.34 (s, 3H), 0.97 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.85, 148.17, 139.88, 136.75, 132.83, 129.11, 129.05, 128.31, 127.95, 127.51, 127.11, 122.23, 121.69, 114.73, 51.78, 49.53, 47.81, 29.97, 29.61, 29.21, 26.36; IR (KBr, ν, cm^{-1}) 2938, 1684, 1592, 1457, 1399, 1268, 1104, 1032, 867, 778; HRMS (APCI-TOF) *m*/*z* calcd for: $C_{22}H_{24}NO$, 318.1858 $[M + H]^+$; found: 318.1850.

5-((4-Chlorophenyl)sulfonyl)-2-ethyl-2,3*a*-dimethyl-1-phenyl-3,3*a*-dihydro-2*H*-cyclopenta[*c*]quinolin-4(5*H*)-one (5l, major). White solid, mp 147–149 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.93–7.90 (m, 4H), 7.51–7.46 (m, 4H), 7.03–6.96 (m, 4H), 6.70 (d, J = 7.2 Hz, 1H), 2.24 (d, J = 14.4 Hz, 1H), 1.90 (d, J = 14.4 Hz, 1H), 1.52–1.49 (m, 2H), 1.33 (s, 3H), 1.17 (s, 3H), 0.95–0.92 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 175.75, 148.29, 140.41, 137.97, 135.52, 134.71, 132.51, 130.28, 129.12, 128.86, 128.39, 127.64, 127.51, 127.27, 126.37, 126.27, 124.03, 54.76, 52.45, 44.89, 32.36, 28.41, 25.09, 8.45; IR (KBr, ν, cm^{-1}) 2966, 1721, 1582, 1478, 1398, 1262, 1187, 1036, 836, 798; HRMS (APCI-TOF) *m*/*z* calcd for: $C_{28}H_{27}NO_3SCl$, 492.1400 $[M + H]^+$; found: 492.1397.

2-Ethyl-2,3*a*,5-trimethyl-1-phenyl-3,3*a*-dihydro-2*H*-cyclopenta-[*c*]quinolin-4(5*H*)-one (5m, major). White solid; mp 157–159 °C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.33–7.29 (m, 3H), 7.17–7.12 (m, 3H), 6.73–6.69 (m, 3H), 3.41 (s, 3H), 2.44 (d, J = 14.0 Hz, 1H), 2.18 (d, J = 14.0 Hz, 1H), 1.65–1.61 (m, 2H), 1.30 (s, 3H), 1.04–1.00 (m, 3H), 0.94 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$; δ, ppm) 175.95, 148.27, 139.77, 136.63, 133.37, 129.38, 128.18, 127.87, 127.51, 127.07, 122.20, 122.18, 114.64, 51.87, 51.84, 44.03, 32.55, 30.05, 26.89, 26.34, 9.90; IR (KBr, ν, cm^{-1}) 2928, 1684, 1593, 1473, 1387, 1273, 1100, 1057, 858, 765; HRMS (APCI-TOF) *m*/*z* calcd for: $C_{23}H_{26}NO$, 332.2014 $[M + H]^+$; found: 332.2010.

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