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COMMUNICATION

NIS-mediated oxidative arene C(sp^2)–H amidation toward 3,4-dihydro-2(^{1}H)-quinolinone, phenanthridone, and *N*-fused spirolactam derivatives

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A new radical-mediated intramolecular arene C(sp^2)–H amidation of 3-phenylpropanamides or [1,1'-biphenyl]-2-carboxamides was developed to prepare a series of 3,4-dihydro-2(^{1}H)-quinolinone and phenanthridone derivatives in moderate to excellent yields (33–94%). Spirolactams could also be obtained using this protocol.

Introduction

Benzo-fused and spiro-fused lactam skeletons are important motifs in many pharmacologically active compounds. The 3,4-dihydro-2(^{1}H)-quinolinone and phenanthridone scaffolds are important members of these classes, and their derivatives are found in many natural products and medicinally active compounds (Figure 1).[1]

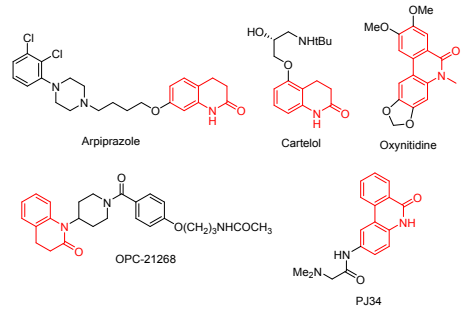
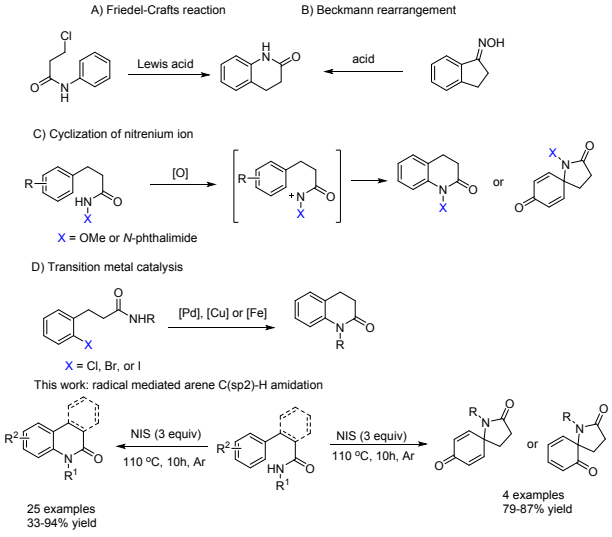


Figure 1 Examples of natural products and medicinally active compounds containing 3,4-dihydro-2(1H)-quinolinone and phenanthridone scaffolds.

Generally, the synthesis of 3,4-dihydro-2(^{1}H)-quinolinones relies on electrophilic aromatic substitution reactions, including the Friedel–Crafts reaction (Scheme 1a),[2a] the Beckmann rearrangement of indanone oxime (Scheme 1b),[2b] and the electrophilic cyclization of nitrenium ions (Scheme 1c).[2c,d] However, these methods require a stoichiometric amount of metal salt. Furthermore, these reactions are limited to primary or secondary amide substrates with methoxy or *N*-phthalimide substituents on the nitrogen atom. The transition-metal-catalyzed arene amidation of aryl halides has provided a convenient method for the synthesis of 3,4-dihydro-2(^{1}H)-quinolinones. Furthermore, remarkable advances have been achieved in the palladium,[3a–d] copper,[3e] and iron catalysis[3f] of this type of transformation (Scheme 1d). Nevertheless, exploring direct intramolecular arene C(sp^2)–H amidation, which avoids prefunctionalization, for the synthesis of these derivatives with high step efficiency and wide substrate scope remains a necessary and challenging task. Compared with established methods, the construction of lactams using *N*-centered amidyl radicals might be a straightforward approach. Recently, some elegant modifications of the Hofmann–Löffler–Freytag (HLF)[4] reaction for the C(sp^3)–H functionalization of amides[5] have been developed. However, the cyclic amination of aromatics using a HLF-type reaction has seen little exploration.[6] Herein, we report a novel synthetic route for the construction benzolactams and spiro-fused lactams through intramolecular arene C(sp^2)–H amidation using an amidyl radical.



Scheme 1 General methods for the synthesis of 3,4-dihydro-2(1*H*)-quinolinones.

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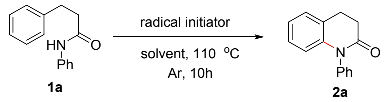
Table 1 Optimization of reaction conditions.[a]



Entry	Radical initiator	Amount (equiv.)	Solvent	Yield (%)[b]
1	NIS	2.0	DCE	65
2	NBS	2.0	DCE	trace
3	NCS	2.0	DCE	0
4	$PhI(OAc)_2 + I_2$	1.5 + 1.5	DCE	trace
5	NIS	2.5	DCE	78
6	**NIS**	**3.0**	**DCE**	**86**
7	NIS	3.0	toluene	61
8	NIS	3.0	CH_3CN	54
9	NIS	3.0	DMF	23
10[c]	NIS	3.0	DCE	79

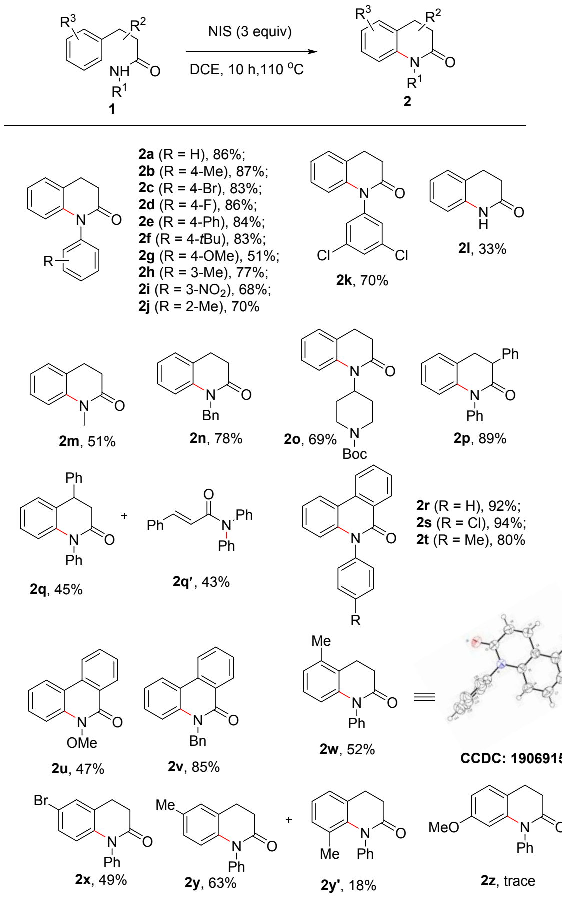
[a] Reaction was conducted on 0.25-mmol scale. [b] Isolated yield.
[c] Reaction was conducted in air.

Results and discussion

Our initial efforts to trigger the metal-free C–H amidation reaction were guided by conditions used for the radical C–H amination of sulfonamides[5b] and amides[5e]. *N*,3-Diphenylpropanamide (**1a**) was selected as a model substrate and stirred in 1,2-dichloroethane (DCE) at 110 °C under an Ar atmosphere to investigate reaction optimization. Oxidants *N*-iodosuccinimide (NIS), *N*-bromosuccinimide (NBS), and *N*-chlorosuccinimide (NCS) were tested initially, with only NIS affording amidation product **2a** in 65% yield (Table 1, entries 1–3). The combination of $PhI(OAc)_2$ and I_2 did not facilitate the desired reaction (entry 4). When the amount of NIS was increased to 3 equiv., an improved 86% yield was obtained (Table 1, entry 6). The solvent was also crucial to this transformation. Using toluene, *N,N*-dimethylformamide (DMF), and CH_3CN as solvent did not further improve the reaction yield (entries 7–9). The yield of **2a** was slightly lower when the reaction was conducted under air (entry 10).

With optimal conditions in hand (Table 1, entry 6), we next examined the extent and generality of this transformation (Table 2). The influence of substituents on the phenyl group attached to the N atom was examined first. *Para*-substituents with different electronic properties were well tolerated in the reaction, affording 3,4-dihydro-2(^{1}H)-quinolinones **2a**–**2g** in good to excellent yields. *Meta*- and *ortho*-substituents afforded desired products **2h**, **2i** and **2j**, respectively, in good yields. Polysubstituted arene (**1K**) was also compatible with this protocol. Under the optimized conditions, the primary amide was also tolerated, but afforded a lower yield (**2l**, 33%). With Me- (**2m**), Bn- (**2n**), or *N*-protected piperidyl (**2o**) substituents on the nitrogen atom, the reactions proceeded smoothly with moderate yields. Notably, **2o** could be further converted into OPC-21268, an orally bioavailable arginine vasopressin (AVP) V_1 antagonist with high V_1 specificity.[1g] A phenyl group on the carbonyl α-position did not significantly influence the reaction, affording product **2p**. However, when two phenyl groups were attached at the carbonyl β-position, the anticipated cyclization product **2q** was obtained in moderate yield, while unexpected product **2q'**, resulting from aryl migration from carbon to the nitrogen center, was also produced.[7] Using this established method, phenanthridinone derivatives **2r**–**2v** bearing different substituents on the nitrogen atom were synthesized in moderate to excellent yields. Furthermore, the removal of the Bn group of **2n** and **2v** proceeded under acidic conditions to give N–H 3,4-dihydro-2(^{1}H)-quinolinone **2l** and phenanthridone **3** according to previously described procedures[11]. Next, substituents on the phenyl ring attached to the alkyl moiety were investigated. *N*-Phenyl-3-(*o*-tolyl)propanamide and 3-(3-bromophenyl)-*N*-phenylpropanamide afforded amidation products **2w** and **2x** in moderate yields. Product **2w** was unambiguously confirmed by X-ray crystallography.[10] For *meta*-Me substituted substrate **1y,** *para*-amidation product **2y** was obtained in moderate yield, accompanied by a small amount of *ortho*-amidation product **2y'**. However, 3-(4-methoxyphenyl)propanamide failed to afford desired product **2z**.

Table 2 Substrate scope for intramolecular C–H amidation.[a,b]



[a] Reaction conditions: **1** (0.25 mmol, 1.0 equiv.) and NIS (0.75 mmol, 3.0 equiv.) in DCE (2 mL) at 110 °C under Ar. [b] Isolated product yields.

When the substrates were changed to TBS-protected phenol derivatives, spirolactams were produced, which are also synthetic and medicinal intermediates (Scheme 2).[8] Pleasingly, the dearomative spirocyclization of Ph- and Bn-protected amides (**2aa** and **2ab**) proceeded in an efficient manner, in contrast to most classical approaches, which require specific N-protecting groups, such as MeO or *N*-phthalimide,[9] or proceed through the oxidation

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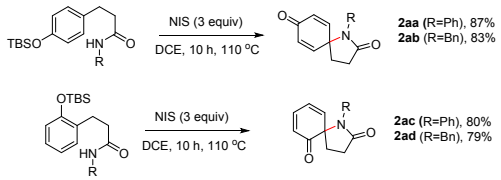
of phenolic oxazolines.[8] To our knowledge, this represents the first synthetic approach to spirolactams using an amidyl radical process. Similarly, *ortho*-substituted phenol derivatives **1ac** and **1ad** underwent cyclization smoothly to afford spirolactams. This protocol not only provides a concise method for the construction of novel spirolactams, but also complements previous work.

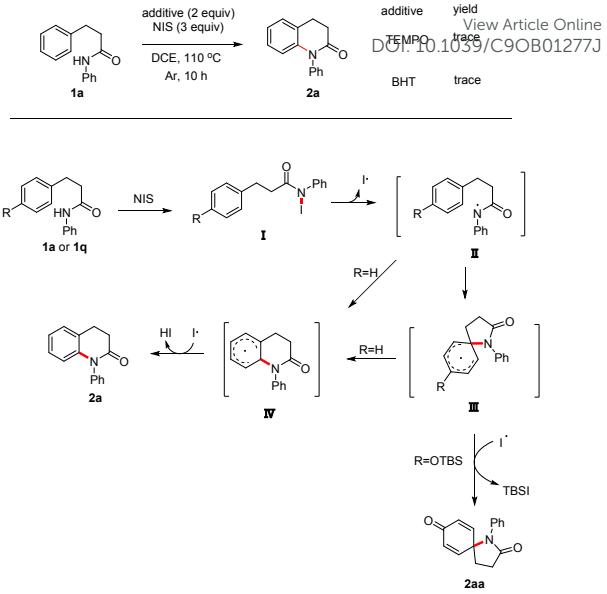
Scheme 2 Synthesis of spirolactams through *ipso*-amidation.[a,b]



[a]Reaction conditions: **1** (0.25 mmol, 1.0 equiv.) and NIS (0.75 mmol, 3.0 equiv.) in DCE (2 mL) at 110 °C under Ar. [b] Isolated product yields.

As shown in Scheme 3, control experiments showed that the oxidative arene C(sp^2)–H amidation of amide **1a** was impeded in the presence of radical inhibitors (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) and butylated hydroxytoluene (BHT). Similarly, When 2 equivalents of TEMPO were added to the solution of **1aa** and NIS in DCE, the reactions were suppressed. In order to further understand this transformation, mass spectrom-etryexperiments of **1a** had been done by adding 2.0 equiv of BHT under the model reaction. The product of the radical captured by BHT were observed via HRMS detection (for details, see the Supporting Information). These results indicated that this arene C(sp^2)–H amidation might proceed *via* a radical pathway. Based on the above results and literature reports,[5,6] a mechanism was proposed for this transformation (Scheme 3). Amides **1a** or **1aa** first react with NIS to give *N*-iodinated compound **I**, which undergoes N–I homolytic cleavage to afford amide N radical **II** under thermal conditions. Radical **II** then undergoes a *5-exo* cyclization onto the aromatic ring to give spiro intermediate **III** or a *6-endo* cyclization to give benzolactam intermediate **IV**, which might also be obtained from intermediate **III** through ring-expansion *via* C–N bond migration. Product **2a** is then produced by the rearomatization of radical **IV**. When the R substituent is OTBS, intermediate **III** affords spirolactam **2aa**.

Scheme 3 Control experiments and possible reaction mechanism.



Conclusions

In conclusion, a novel and efficient NIS-mediated radical oxidative arene C(sp^2)–H amidation has been developed to synthesize 3,4-dihydro-2(^{1}H)-quinolinone and phenanthridone derivatives in moderate to excellent yields. Differently substituted 3-phenylpropanamides or [1,1'-biphenyl]-2-carboxamides were tolerated. Furthermore, spirolactams bearing Ph or Bn as *N*-substituents were readily obtained using this protocol.

EXPERIMENTAL SECTION

General Method and Materials. All reagents were used as received. Acetonitrile was distilled on phosphorus pentoxide. ^{1}H and ^{13}C Nuclear Magnetic Resonance (NMR) spectra were recorded on Bruker Avance 400 Ultrashield NMR spectrometers. Chemical shifts (δ) were given in parts per million (ppm) and were measured downfield from internal tetramethylsilane. High-resolution mass spectrometry (HRMS) data were obtained on an FTICR-MS instrument (Ionspec 7.0 T). The melting points were determined on an X-4 microscope melting point apparatus and are uncorrected. Conversion was monitored by thin layer chromatography (TLC). Flash column chromatography was performed over silica gel (100-200 mesh). NH free 3,4-dihydro-2(1H)-quinolinone **2l** and phenanthridone **3** can obtained from the N-benzyl derivatives with a previously described procedure.[11]

General procedure A for the preparation of compounds 1a-o.

To a solution of amine (5.0 mmol, 1.0 equiv) in dichloromethane (20 mL) was added triethylamine (1.0 mL,7.5 mmol, 1.5 equiv) at 0 ºC. After stirring for 10 min at 0 ºC, 3-phenylpropanoyl chloride (0.47 mL,5.0 mmol, 1.0 equiv) was added dropwise and then the mixture was stirred at room temperature. After completing reaction, the mixture was added 30 mL H_2O. The organic layer was separated and the aqueous layer was extracted with dichloromethane (20mL × 3). The combined organic phase was washed with brine (20 mL), and then dried over Na_2SO_4. After filtration, the solvent was concentrated in vacuo. The products were purified by column chromatography with petroleum ether and ethyl acetate as an eluent.

General procedure B for the preparation of compounds 1p-z.

A mixture of 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (1.04g, 6.5 mmol, 1.3 equiv), DMAP (0.92g, 7.5 mmol, 1.5 equiv), acid (5 mmol, 1.0 equiv), and amine (5 mmol, 1.0 equiv) in CH_2Cl_2 (20 mL) was stirred at room temperature for 4 h. After completing reaction, the mixture was added 30 mL H_2O. The organic layer was separated and the aqueous layer was extracted with dichloromethane (20mL × 3). The combined organic phase was washed with brine (20 mL), and then dried over Na_2SO_4. After filtration, the solvent was concentrated in vacuo. The products were purified by column chromatography with petroleum ether and ethyl acetate as an eluent.

N,3-diphenylpropanamide (1a). According to the general procedure A. White solid (0.98 g, 87%). M.p. = 95-96 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 7.9 Hz, 2H), 7.35 – 7.14 (m, 8H), 7.08 (t, J = 7.4 Hz, 1H), 3.04 (t, J = 7.6 Hz, 2H), 2.64 (t, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 140.7, 137.8, 129.0, 128.7, 128.4, 126.4, 124.3, 120.0, 39.5, 31.6. HRMS (ESI): calcd. for $C_{15}H_{16}NO$ [M + H]$^+$ 226.1226; found 226.1230. Rf 0.3 (Petroleum ether/EtOAc, 5/1).

3-phenyl-N-(p-tolyl)propanamide (1b). According to the general procedure A. White solid (1.0 g, 87%). M.p. =128-130 °C. 1H NMR (400 MHz, CDCl3) δ 7.40 – 7.23 (m, 5H), 7.23 – 7.16 (m, 3H), 7.07 (d, J = 8.1 Hz, 2H), 3.02 (t, J = 7.6 Hz, 2H), 2.61 (t, J = 7.7 Hz, 2H), 2.29 (s, 3H).13C NMR (100 MHz, CDCl3) δ 170.4, 140.7, 135.2, 134.0, 129.5, 128.6, 128.4, 126.4, 120.2, 39.4, 31.6 , 20.9. HRMS (ESI): calcd. for C16H18NO [M + H]+ 240.1383; found 240.1387. Rf 0.3 (Petroleum ether/EtOAc, 5/1).

N-(4-bromophenyl)-3-phenylpropanamide (1c). According to the general procedure A. White solid (1.28 g, 84%). M.p. = 149-151 °C. ^{1}H NMR (400 MHz, CDCl3) δ 7.41 – 7.34 (m, 2H), 7.33 – 7.27 (m, 4H), 7.25 – 7.15 (m, 3H), 3.01 (t, J = 7.6 Hz, 2H), 2.63 (t, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, CDCl3) δ 170.6, 140.4, 136.8, 131.9, 128.7, 128.4, 126.5, 121.6, 116.9, 39.4, 31.5. HRMS (ESI): calcd. for $C_{15}H_{15}BrNO$ [M + H]$^+$ 304.0332; found 304.0327. Rf 0.3 (Petroleum ether/EtOAc, 5/1).

N-(4-fluorophenyl)-3-phenylpropanamide (1d). According to the general procedure A. White solid (1.0 g, 82%). M.p. = 116-118 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.27 (m, 4H), 7.25-7.19(m, 3H), 6.94 (t, J = 8.5 Hz, 2H), 3.02 (t, J = 7.5 Hz, 2H), 2.63 (t, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 159.4 (d, J = 243.6 Hz), 140.6, 133.7, 128.7, 128.4, 126.5, 122.0 (d, J = 7.3 Hz), 115.6 (d, J = 22.5 Hz), 39.3, 31.6. HRMS (ESI): calcd. for $C_{15}H_{15}FNO$ [M + H]$^+$ 224.1132; found 224.1131. Rf 0.3 (Petroleum ether/EtOAc, 5/1).

N-([1,1'-biphenyl]-4-yl)-3-phenylpropanamide (1e). According to the general procedure A. White solid (1.3 g, 84%). M.p. = 176-178 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.46 (m, 6H), 7.41 (t, J = 7.6 Hz, 2H), 7.30 (dd, J = 13.7, 7.2 Hz, 3H), 7.23 (dd, J = 7.5, 3.4 Hz, 3H), 7.19 (s, 1H), 3.06 (t, J = 7.6 Hz, 2H), 2.67 (t, J = 7.6 Hz, 2H).^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 140.6, 140.5, 137.2, 137.0, 128.8, 128.7, 128.4, 127.6, 127.1, 126.9, 126.5, 120.3, 39.52, 31.6. HRMS (ESI): calcd. for $C_{21}H_20NO$ [M + H]$^+$ 302.1539; found 302.1542. Rf 0.3 (Petroleum ether/EtOAc, 5/1).

N-(4-(tert-butyl)phenyl)-3-phenylpropanamide (1f). According to the general procedure A. White solid (1.2 g, 87%). M.p. = 136-138 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 - 7.26 (m, 6H), 7.24 - 7.05 (m, 4H), 3.04 (t, J = 7.6 Hz, 1H), 2.64 (t, J = 7.6 Hz, 1H), 1.29 (s, 9H). 13C NMR (101 MHz, $CDCl_3$) δ 170.3, 147.3, 140.7, 135.1, 128.6, 128.4, 126.3, 125.7, 119.8, 39.4, 34.3, 31.6, 31.3. HRMS (ESI): calcd. for $C_{19}H_{24}NO$ [M + H]$^+$ 282.1852; found 282.1852. Rf 0.2 (Petroleum ether/EtOAc, 5/1).

N-(4-methoxyphenyl)-3-phenylpropanamide (1g). According to the general procedure A. White solid (1.1 g, 86%). M.p. = 128-130 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 4H), 7.25 – 7.19 (m, 3H), 7.06 (s, 1H), 6.89 – 6.66 (m, 2H), 3.77 (s, 3H), 3.04 (t, J = 7.6 Hz, 2H), 2.62 (t, J = 7.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 156.4, 140.7, 130.8, 128.6, 128.4, 126.3, 121.9, 114.1, 99.9, 55.4, 39.3, 31.6.HRMS (ESI): calcd. for $C_{16}H_{18}NO_2$ [M + H]$^+$ 256.1332; found 256.1334. Rf 0.2 (Petroleum ether/EtOAc, 5/1).

3-phenyl-N-(m-tolyl)propanamide (1h). According to the general procedure A. White solid (1.0 g, 85%). M.p. = 73-75 °C. ^{1}H NMR (400 MHz, CDCl3) δ 7.36 – 7.25 (m, 3H), 7.24 – 7.05 (m, 6H), 6.90 (d, J = 6.5 Hz, 1H), 3.04 (t, J = 7.6 Hz, 2H), 2.63 (t, J = 7.6 Hz, 2H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, CDCl3) δ 170.4, 140.7, 138.9, 137.7, 128.8, 128.7, 128.4, 126.4, 125.1, 120.6, 117.0, 39.5, 31.6, 21.5. HRMS (ESI): calcd. for $C_{16}H_{18}NO$ [M + H]$^+$ 240.1383; found 240.1388. Rf 0.33 (Petroleum ether/EtOAc, 5/1).

N-(3-nitrophenyl)-3-phenylpropanamide (1i). According to the general procedure A. Yellow solid (1.1 g, 82%). M.p. = 109-111 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.98 – 7.83 (m, 2H), 7.55 – 7.43 (m, 2H), 7.37 – 7.29 (m, 2H), 7.28 – 7.18 (m, 3H), 3.09 (t, J = 7.5 Hz, 2H), 2.75 (t, J = 7.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 148.4, 140.2, 138.7, 129.8, 128.7, 128.7, 128.3, 128.3, 126.6, 125.5, 118.9, 114.5, 39.3, 31.3. HRMS (ESI): calcd. for $C_{15}H_{15}N_2O_3$ [M + H]$^+$ 271.1077; found 271.1077. Rf 0.3 (Petroleum ether/EtOAc, 5/1).

3-phenyl-N-(o-tolyl)propanamide (1j). According to the general procedure A. White solid (1.1 g, 90%). M.p. = 118-120 °C.1H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 7.3 Hz, 1H), 7.36 – 7.16 (m, 7H), 7.09 (t, J = 7.2 Hz, 1H), 6.92 (s, 1H), 3.10 (t, J = 7.3 Hz, 2H), 2.74 (t, J = 7.3 Hz, 2H), 2.09 (s, 3H).13C NMR (100 MHz, CDCl3) δ 170.4, 140.6, 135.5, 130.4, 128.7, 128.5, 126.7, 126.5, 125.3, 123.4, 39.3, 31.8, 17.6. HRMS (ESI): calcd. for $C_{16}H_{18}NO$ [M + H]$^+$ 240.1383; found 240.1386. Rf 0.4 (Petroleum ether/EtOAc, 5/1).

N-(3,5-dichlorophenyl)-3-phenylpropanamide (1k). According to the general procedure A. Grey solid (1.29 g, 89%). M.p. = 97-99 °C. 1H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.27 (m, 5H), 7.25 – 7.17 (m, 3H), 7.06 (s, 1H), 3.02 (t, J = 7.5 Hz, 2H), 2.65 (t, J = 7.5 Hz, 2H). 13C NMR (101 MHz, $CDCl_3$) δ 170.7, 140.2, 139.4, 135.1, 128.7, 128.3, 126.5, 124.2, 118.1, 39.3, 31.3. HRMS (ESI): calcd. for $C_{15}H_{14}Cl_2NO$ [M + H]$^+$ 294.0447; found 294.0443. Rf 0.3 (Petroleum ether/EtOAc, 5/1).

3-phenylpropanamide (1l). According to the general procedure A. White solid (0.57 g, 76%). M.p. = 99-101 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.25 (m, 2H), 7.24 – 7.16 (m, 3H), 5.76 (s, 1H), 5.46 (s, 1H), 2.96 (t, J = 7.8 Hz, 2H), 2.52 (t, J = 7.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.7, 140.7, 128.6, 128.3, 126.3, 37.5, 31.4. HRMS (ESI): calcd. for $C_9H_{12}NO$ [M + H]$^+$ 150.0913; found 150.0913. Rf 0.2 (Petroleum ether/EtOAc, 1/1).

N-methyl-3-phenylpropanamide (1m). According to the general procedure A. Colorless solid (0.73 g, 90%). M.p. = 58-60 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (dd, J = 10.0, 5.1 Hz, 2H), 7.19 (t, J = 6.3 Hz, 3H), 5.60 (s, 1H), 2.96 (t, J = 7.8 Hz, 2H), 2.75 (s, 3H), 2.51 – 2.38 (m, 2H).^{13}C NMR (100 MHz, $CDCl_3$) δ 172.8, 141.0, 128.5, 128.3, 126.2, 38.4, 31.8, 26.3. HRMS (ESI): calcd. for $C_{10}H_{14}NO$ [M + H]$^+$ 164.1070; found 164.1073. Rf 0.2 (Petroleum ether/EtOAc, 2/1).

N-benzyl-3-phenylpropanamide (1n). According to the general procedure A. White solid (0.98 g, 87%). M.p. = 83-84 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.23 (m, 5H), 7.23 – 7.15 (m, 3H), 7.15 – 7.08 (m, 2H), 5.82 (s, 1H), 4.36 (d, J = 5.5 Hz, 2H), 2.97 (t, J = 7.6 Hz, 2H), 2.49 (t, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 140.8, 138.2, 128.7, 128.6, 128.4, 127.7, 127.5, 126.3, 43.6, 38.5, 31.7. HRMS (ESI): calcd. for $C_{16}H_{18}NO$ [M + H]$^+$ 240.1383; found 240.1384. Rf 0.3 (Petroleum ether/EtOAc, 2/1).

tert-butyl 4-(3-phenylpropanamido)piperidine-1-carboxylate (1o). According to the general procedure A. White solid (1.2 g, 73%). M.p. = 141-143 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.14 (m, 5H), 4.15 – 3.72 (m, 3H), 2.95 (t, J = 7.5 Hz, 2H), 2.80 (s, 2H), 2.45 (t, J =

7.6 Hz, 2H), 1.79 (d, J = 11.9 Hz, 2H), 1.44 (s, 9H), 1.25 – 1.08 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 154.7, 140.8, 128.5, 128.4, 126.3, 79.6, 46.5, 38.6, 32.0, 31.8, 28.4. HRMS (ESI): calcd. for $C_{19}H_{29}N_2O_3$ $[M + H]^+$ 355.1992; found 355.1988 . Rf 0.3 (Petroleum ether/EtOAc, 3/1).

N,2,3-triphenylpropanamide (1p). According to the general procedure B. White solid (1.3 g, 84%). M.p. = 167-168 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.26 (m, 6H), 7.24 – 7.09 (m, 8H), 7.03 (t, J = 7.3 Hz, 1H), 3.74 (t, J = 7.4 Hz, 1H), 3.60 (dd, J = 13.5, 7.8 Hz, 1H), 3.04 (dd, J = 13.5, 7.0 Hz, 1H).^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 139.5, 139.2, 137.7, 129.1, 129.0, 128.9, 128.4, 128.1, 127.6, 126.4, 124.4, 120.0, 56.5, 39. HRMS (ESI): calcd. for $C_{21}H_20NO$ $[M + H]^+$ 302.1539; found 302.1541. Rf 0.3 (Petroleum ether/EtOAc, 5/1).

N,3,3-triphenylpropanamide (1q). According to the general procedure B. White solid (1.4 g, 90%). M.p. = 175-177 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (t, J = 8.4 Hz, 11H), 7.25 – 7.20 (m, 3H), 7.06 (d, J = 6.6 Hz, 1H), 6.94 (s, 1H), 4.64 (t, J = 7.7 Hz, 1H), 3.08 (d, J = 7.7 Hz, 2H).^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 143.5, 137.5, 128.9, 128.8, 127.8, 126.7, 124.4, 120.1, 47.5, 44.4. HRMS (ESI): calcd. for $C_{21}H_20NO$ $[M + H]^+$ 302.1539; found 302.1536. Rf 0.3 (Petroleum ether/EtOAc, 5/1).

N-phenyl-[1,1'-biphenyl]-2-carboxamide (1r). According to the general procedure B. White solid (1.1 g, 83%). M.p. = 104-106 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 7.4 Hz, 1H), 7.60 – 7.33 (m, 8H), 7.22 (dd, J = 14.5, 6.7 Hz, 2H), 7.10 (d, J = 7.8 Hz, 2H), 7.04 (t, J = 7.3 Hz, 1H), 6.98 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 140.0, 139.6, 137.6, 135.3, 130.7, 130.4, 129.6, 129.0, 128.9, 128.1, 127.9, 124.4, 120.0. HRMS (ESI): calcd. for $C_{19}H_{16}NO$ $[M + H]^+$ 274.1226; found 274.1232. Rf 0.4 (Petroleum ether/EtOAc, 5/1).

N-(4-chlorophenyl)-[1,1'-biphenyl]-2-carboxamide (1s). According to the general procedure B. White solid (1.3 g, 86%). M.p. = 160-162 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (dd, J = 7.6, 1.1 Hz, 1H), 7.35 (td, J = 7.5, 1.4 Hz, 1H), 7.31 – 7.16 (m, 7H), 7.02 – 6.89 (m, 2H), 6.90 – 6.80 (m, 2H), 6.71 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 139.8, 139.5, 136.1, 134.9, 130.9, 130.3, 129.6, 129.3, 129.0, 128.8, 128.2, 128.0, 121.0. HRMS (ESI): calcd. for $C_{19}H_{15}ClNO$ $[M + H]^+$ 308.0837; found 308.0835. Rf 0.2 (Petroleum ether/EtOAc, 5/1).

N-(p-tolyl)-[1,1'-biphenyl]-2-carboxamide (1t). According to the general procedure B. White solid (1.25 g, 87%). M.p. = 136-138 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J = 7.6 Hz, 1H), 7.82 – 7.60 (m, 8H), 7.25 (q, J = 8.4 Hz, 4H), 7.10 (s, 1H), 2.51 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 140.0, 139.5, 135.4, 134.9, 134.0, 130.6, 130.3, 129.5, 129.3, 128.9, 128.8, 128.0, 127.9, 120.0, 20.8. HRMS (ESI): calcd. for $C_{20}H_{18}NO$ $[M + H]^+$ 288.1383; found 288.1382. Rf 0.2 (Petroleum ether/EtOAc, 5/1).

N-methoxy-[1,1'-biphenyl]-2-carboxamide (1u). According to the general procedure B. White solid (1.1 g, 83%). M.p. = 99-101 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 7.85 (m, 1H), 7.63 (s, 1H), 7.51 (t, J = 7.5 Hz, 1H), 7.45 – 7.36 (m, 7H), 3.51 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 140.0, 139.7, 132.3, 130.8, 130.1, 129.2, 128.8, 128.7 ,128.1, 127.7, 63.9. HRMS (ESI): calcd. for $C_{14}H_{14}NO_2$ $[M + H]^+$ 228.1019; found 228.1021. Rf 0.3 (Petroleum ether/EtOAc, 3/1).

N-benzyl-[1,1'-biphenyl]-2-carboxamide (1v). According to the general procedure B. White solid (1.2 g, 83%). M.p. = 96-98 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 7.5 Hz, 1H), 7.59 – 7.30 (m, 8H), 7.25 (dd, J = 14.1, 11.9 Hz, 3H), 7.01 – 6.77 (m, 2H),5.51 (s, 1H), 4.36 (d, J = 5.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 140.3, 139.5, 137.5, 135.6, 130.20, 130.1, 128.9, 128.8 128.7, 128.6, 127.8, 127.7, 127.4, 44.2. HRMS (ESI): calcd. for $C_{20}H_{18}NO$ $[M + H]^+$ 288.1383; found 288.1388. Rf 0.42 (Petroleum ether/EtOAc, 5/1).

N-phenyl-3-(o-tolyl)propanamide (1w). According to the general procedure B. White solid (1.0 g, 84%). M.p. = 96-98 °C.1H ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.40 (m, 3H), 7.38 – 7.29 (m, 2H), 7.23 – 7.07 (m, 5H), 3.07 (t, J = 7.8 Hz, 2H), 2.65 (t, J = 7.8 Hz, 2H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ170.8, 138.8, 137.9, 136.1, 130.5, 129.0, 128.7, 126.5, 126.3, 124.3, 120.1, 38.1, 28.8, 19.4. HRMS (ESI): calcd. for $C_{16}H_{18}NO$ $[M + H]^+$ 240.1383; found 240.1386. Rf 0.3 (Petroleum ether/EtOAc, 5/1).

3-(3-bromophenyl)-N-phenylpropanamide (1x). According to the general procedure B. White solid (1.3 g, 83%). M.p. = 91-93 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.48 (d, J = 7.9 Hz, 2H), 7.43 – 7.24 (m, 4H), 7.24 – 7.05 (m, 3H), 3.00 (t, J = 7.7 Hz, 2H), 2.63 (t, J = 7.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ169.9, 143.0, 137.8, 130.2, 129.2, 128.9, 128.6, 125.8, 124.5, 120.6, 119.9, 31.9, 25.2. HRMS (ESI): calcd. for $C_{15}H_{16}BrNO$ $[M + H]^+$ 304.0332; found 304.0331. Rf 0.3 (Petroleum ether/EtOAc, 5/1).

N-phenyl-3-(m-tolyl)propanamide (1y). According to the general procedure B. White solid (1.0 g, 87%). M.p. = 70-72 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, J = 7.6 Hz, 3H), 7.31 (dd, J = 13.6, 5.6 Hz, 2H), 7.25 – 7.09 (m, 5H), 3.07 (t, J = 7.8 Hz, 2H), 2.65 (t, J = 7.8 Hz, 2H), 2.36 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 138.8, 137.9, 136.1, 130.5, 129.0, 128.7, 126.5, 126.3, 124.3, 120.1, 38.1, 28.84, 19.4. HRMS (ESI): calcd. for $C_{16}H_{18}NO$ $[M + H]^+$ 240.1383; found 240.1383. Rf 0.3 (Petroleum ether/EtOAc, 5/1).

3-(4-methoxyphenyl)-N-phenylpropanamide (1z). According to the general procedure B. White solid (0.97 g, 76%). M.p. = 127-129 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.18 (m, 5H), 7.13 – 7.05 (m, 3H), 6.89 -6.70 (m, 2H), 3.76 (s, 3H), 2.96 (t, J = 7.2 Hz, 2H), 2.60 (t, J = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 158.1, 137.8, 132.7, 129.4, 128.9, 124.3, 120.0, 114.0, 55.3, 39.7, 30.7. HRMS (ESI): calcd. for $C_{16}H_{18}NO_2$ $[M + H]^+$ 256.1332; found 256.1335. Rf 0.4 (Petroleum ether/EtOAc, 5/1).

3-(4-((tert-butyldimethylsilyl)oxy)phenyl)-N-phenylpropanamide (1aa). According to the general procedure B. White solid (1.6 g, 89%). M.p. = 117-119 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 7.8 Hz, 2H), 7.28 (dd, J = 13.1, 5.1 Hz, 2H), 7.08 (d, J = 7.4 Hz, 4H), 6.76 (d, J = 8.2 Hz, 2H), 2.97 (t, J = 7.5 Hz, 2H), 2.61 (t, J = 7.5 Hz, 2H), 0.97 (s, 9H), 0.18 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9, 138.4, 133.9, 130.0, 129.7, 125.0, 120.9, 120.6, 40.5, 31.6, 26.4, 18.9, 3.7. HRMS (ESI): calcd. for $C_{21}H_{30}NO_2Si$ $[M + H]^+$ 256.2040; found 256.2042. Rf 0.4 (Petroleum ether/EtOAc, 5/1).

N-benzyl-3-(4-((tert-butyldimethylsilyl)oxy)phenyl)propanamide (1ab). According to the general procedure B. White solid (1.6 g, 85%). M.p. = 80-82 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 3H), 7.19 (d, J = 7.1 Hz, 2H), 7.07 (d, J = 8.3 Hz, 2H), 6.77 (d, J = 8.3 Hz, 2H), 5.63 (s, 1H), 4.42 (d, J = 5.6 Hz, 2H), 2.95 (t, J = 7.5 Hz, 2H), 2.50 (t, J = 7.6 Hz, 2H), 1.01 (s, 9H), 0.21 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 154.1, 138.2, 133.4, 129.3, 128.7, 127.8, 127.5, 120.1, 43.6, 38.8, 31.0, 25.7, 18.2, 4.4. HRMS (ESI): calcd. for $C_{22}H_{32}NO_2Si$ $[M + H]^+$ 370.2197; found .370.2200. Rf 0.2 (Petroleum ether/EtOAc, 5/1).

3-(2-((tert-butyldimethylsilyl)oxy)phenyl)-N-phenylpropanamide (1ac). According to the general procedure B. Yellow oil (1.4 g, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 8.0 Hz, 2H), 7.32 – 7.21 (m, 3H), 7.11 (ddd, J = 24.7, 16.2, 7.4 Hz, 3H), 6.87 (t, J = 7.1 Hz, 1H), 6.81 (d, J = 8.0 Hz, 1H), 3.00 (t, J = 7.6 Hz, 2H), 2.63 (t, J = 7.6 Hz, 2H), 1.02 (s, 9H), 0.24 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 153.6, 137.9, 131.1, 130.5, 128.9, 127.6, 124.2, 121.5, 120.0, 118.7, 37.8, 26.7, 25.9, 18.3, 4.1. HRMS (ESI): calcd. for $C_{21}H_30NO_2Si$ $[M + H]^+$ 356.2040; found 356.2044. Rf 0.3 (Petroleum ether/EtOAc, 5/1).

N-benzyl-3-(2-((tert-butyldimethylsilyl)oxy)phenyl)propanamide (1ad). According to the general procedure B. Yellow oil (1.3 g, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.21 (m, 3H), 7.12 (dt, J = 15.5,

6.6 Hz, 4H), 6.87 (t, J = 7.3 Hz, 1H), 6.77 (d, J = 8.0 Hz, 1H), 5.69 (s, 1H), 4.39 (d, J = 5.6 Hz, 2H), 2.96 (t, J = 7.6 Hz, 2H), 2.51 (t, J = 7.6 Hz, 2H), 0.99 (s, 9H), 0.22 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 153.5, 138.3, 131.2, 130.5, 128.6, 127.7, 127.4, 121.4, 118.6, 43.5, 36.8, 26.8, 25.8, 18.2, 4.1. HRMS (ESI): calcd. for $C_{21}H_{32}NO_2Si$ [M + H]$^+$ 370.2197; found 370.2201. Rf 0.22 (Petroleum ether/EtOAc, 5/1).

General experimental procedure for 2.

A mixture of amide 1 (0.25 mmol, 1.0 equiv), NIS (169 mg, 0.75 mmol, 3 equiv) in 1,2-dichloroethane (2 mL) in pressure tube (purged with Ar) was heated at 110 oC for 10 hours. Upon completion, the reaction mixture was cooled to room temperature. The reaction mixture was diluted with 30 mL dichloromethane and then treated with saturated aqueous $Na_2S_2O_3$ solution. Aqueous phase was extracted with dichloromethane twice. Combined organic phases were dried with Na_2SO_4. The solvents were removed under reduced pressure and the resulting mixture was purified by flash column chromatography (silica gel, hexane/EtOAc 5/1).

1-phenyl-3,4-dihydroquinolin-2(1H)-one (2a). White solid (47.9 mg, 86%). M.p. = 227-229 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (t, J = 7.6 Hz, 2H), 7.42 (t, J = 7.4 Hz, 1H), 7.29-7.15 (m, 3H), 7.05 – 6.95 (m, 2H), 6.35 (d, J = 7.9 Hz, 1H), 3.19 – 3.00 (m, 2H), 2.82 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 141.7, 138.5, 129.9, 129.1, 128.2, 127.8, 127.2, 125.7, 123.0, 117.1, 32.3, 25.7. HRMS (ESI): calcd. for $C_{15}H_{14}NO$ [M + H]$^+$ 224.1070; found 224.1077.

1-(p-tolyl)-3,4-dihydroquinolin-2(1H)-one (2b). White solid (51.5 mg, 87%). M.p. = 144-146 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 7.1 Hz, 1H), 7.12 (d, J = 8.2 Hz, 2H), 7.01 – 6.99 (m, 1H), 6.96 (td, J = 7.4, 1.0 Hz, 1H), 6.39 (d, J = 8.0 Hz, 1H), 3.07 – 2.97 (m, 2H), 2.89-2.77 (m, 2H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 141.8, 138.1, 135.7, 130.6, 128.7, 127.8, 127.1, 125.6, 122.9, 117.0, 32.3, 25.7, 21.3. HRMS (ESI): calcd. for $C_{16}H_{16}NO$ [M + H]$^+$ 238.1226; found 238.1230.

1-(4-bromophenyl)-3,4-dihydroquinolin-2(1H)-one (2c). White solid (62.7 mg, 83%). M.p. = 194-196 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.55 (m, 2H), 7.21 (d, J = 7.2 Hz, 1H), 7.15 – 7.10 (m, 2H), 7.08 – 7.04 (m, 1H), 7.02 – 6.98 (m, 1H), 6.37 (d, J = 8.0 Hz, 1H), 3.13 – 2.97 (m, 2H), 2.86 – 2.78 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 141.3, 137.5, 133.1, 130.8, 128.0, 127.3, 125.8, 123.3, 122.1, 116.9, 32.2, 25.6. HRMS (ESI): calcd. for $C_{15}H_{13}BrNO$ [M + H]$^+$ 302.0175; found 302.0176.

1-(4-fluorophenyl)-3,4-dihydroquinolin-2(1H)-one (2d). White solid (51.8 mg, 86%). M.p. = 124-126 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.13 (m, 5H), 7.09 – 7.03 (m, 1H), 7.02 – 6.95 (m, 1H), 6.35 (d, J = 8.0 Hz, 1H), 3.11 – 3.01 (m, 2H), 2.87 – 2.77 (m, 2H); 13C NMR (100 MHz, $CDCl_3$) δ170.3, 162.08 (d, J = 247.6 Hz), 141.5, 134.2 (d, J = 3.1 Hz), 130.7 (d, J = 8.6 Hz), 127.9, 127.2, 125.7, 123.1, 116.90 (d, J = 11.2 Hz), 116.7, 32.2, 25.6. HRMS (ESI): calcd. for $C_{15}H_{13}FNO$ [M + H]$^+$ 242.0976; found 242.0975.

1-([1,1'-biphenyl]-4-yl)-3,4-dihydroquinolin-2(1H)-one (2e). White solid (62.9 mg, 84%). M.p. = 174-176 °C. 1H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.69 (m, 2H), 7.65 – 7.59 (m, 2H), 7.46 (t, J = 7.6 Hz, 2H), 7.37 (t, J = 7.3 Hz, 1H), 7.31 (d, J = 8.3 Hz, 2H), 7.22 (d, J = 7.3 Hz, 1H), 7.11 – 7.03 (m, 1H), 7.00 (dd, J = 7.3, 6.4 Hz, 1H), 6.46 (d, J = 8.0 Hz, 1H), 3.12 – 3.06 (m, 2H), 2.89 – 2.82 (m, 2H); 13C NMR (100 MHz, $CDCl_3$) δ 170.3, 141.6, 141.1, 140.3, 137.6, 129.3, 128.8, 128.6, 127.8, 127.6, 127.3, 127.2, 125.8, 123.1, 117.1, 32.3, 25.7. HRMS (ESI): calcd. for $C_{21}H_{18}NO$ [M + H]$^+$ 300.1383; found 300.1388.

1-(4-(tert-butyl)phenyl)-3,4-dihydroquinolin-2(1H)-one (2f). Colorless oil (58.4 mg 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.47 (m, 2H), 7.20 (d, J = 7.3 Hz, 1H), 7.17 – 7.11 (m, 2H), 7.04 (td, J = 7.9, 1.6 Hz, 1H), 6.97 (td, J = 7.4, 1.2 Hz, 1H), 6.38 (dd, J = 8.0, 0.8 Hz, 1H), 3.21 – 2.99 (m, 2H), 2.89 – 2.73 (m, 2H), 1.36 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 150.9, 141.8, 135.6, 128.3, 127.7, 127.1, 126.8, 125.6, 122.8, 117.1, 34.7, 32.3, 31.4, 25.6. HRMS (ESI): calcd. for $C_{19}H_{22}NO$ [M + H]$^+$ 280.1696; found 280.1698. Rf 0.2 (Petroleum ether/EtOAc, 5/1).

1-(4-methoxyphenyl)-3,4-dihydroquinolin-2(1H)-one (2g). White solid (29.4 mg 46%). M.p. = 160-162 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 - 7.22 (m, 1H), 7.18 - 7.14 (m, 2H), 7.10 – 6.95 (m, 4H), 6.42 (d, J = 8.0 Hz, 1H), 3.88 (s, 3H), 3.13 – 3.04 (m, 2H), 2.89 – 2.80 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 159.1, 141.9, 130.9, 129.9, 127.7, 127.1, 125.5, 122.8, 116.9, 115.1, 55.4, 32.2, 25.6. HRMS (ESI): calcd. for $C_{16}H_{16}NO_2$ [M + H]$^+$ 254.1176; found 254.1177. Rf 0.2 (Petroleum ether/EtOAc, 5/1).

1-(m-tolyl)-3,4-dihydroquinolin-2(1H)-one (2h). White solid (45.6 mg, 77%). M.p. = 62-63 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (t, J = 7.6 Hz, 1H), 7.24 – 7.18 (m, 2H), 7.03 (d, J = 8.5 Hz, 3H), 6.98 (t, J = 7.2 Hz, 1H), 6.37 (d, J = 7.9 Hz, 1H), 3.11 – 3.01 (m, 2H), 2.87 – 2.77 (m, 2H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 141.7, 139.9, 138.3, 129.6, 129.6, 129.5, 127.7, 127.1, 125.9, 125.6, 122.9, 117.0, 32.2, 25.7, 21.4. HRMS (ESI): calcd. for $C_{16}H_{16}NO$ [M + H]$^+$ 238.1226; found 238.1231.

1-(3-nitrophenyl)-3,4-dihydroquinolin-2(1H)-one (2i). Yellow oil (46.2 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, J = 7.3 Hz, 1H), 8.19 (d, J = 1.9 Hz, 1H), 7.85 – 7.55(m, 2H), 7.31 – 7.26 (m, 1H), 7.09 (p, J = 7.3 Hz, 1H), 6.35 (d, J = 7.5 Hz, 1H), 3.13 (t, J = 7.1 Hz, 2H), 2.88 (t, J = 7.1 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 149.2, 140.8, 139.7, 135.6, 130.6, 128.2, 127.4, 126.1, 124.6, 123.7, 123.0, 116.8, 32.1, 25.5. HRMS (ESI): calcd. for $C_{15}H_{13}N_2O_3$ [M + H]$^+$ 269.0921; found 269.0919. Rf 0.2 (Petroleum ether/EtOAc, 5/1).

1-(o-tolyl)-3,4-dihydroquinolin-2(1H)-one (2j). White solid (41.5 mg, 70%). M.p. = 84-86 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.29 (m, 3H), 7.25 – 7.20 (m, 1H), 7.14 (d, J = 6.6 Hz, 1H), 7.01 (dd, J = 13.2, 7.5 Hz, 2H), 6.24 (d, J = 7.9 Hz, 1H), 3.08 (t, J = 7.4 Hz, 2H), 2.84 (t, J = 7.2 Hz, 2H), 2.08 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 140.8, 137.1, 136.5, 131.4, 129.2, 128.7, 127.8, 127.5, 127.3, 125.4, 122.9, 116.2, 32.0, 25.7, 17.4. HRMS (ESI): calcd. for $C_{16}H_{16}NO$ [M + H]$^+$ 238.1226; found 238.1229.

1-(3,5-dichlorophenyl)-3,4-dihydroquinolin-2(1H)-one (1k). Colorless oil (61.4 mg 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (s, 1H), 7.24 – 7.15 (m, 3H), 7.10 (t, J = 7.6 Hz, 1H), 7.03 (t, J = 7.3 Hz, 1H), 6.38 (d, J = 8.0 Hz, 1H), 3.06 (t, J = 7.2 Hz, 2H), 2.86 – 2.68 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.0, 140.8, 140.3, 135.8, 128.6, 128.0, 128.0, 127.4, 125.8, 123.6, 116.9, 32.1, 25.5. HRMS (ESI): calcd. for $C_{19}H_{13}ClNO$ [M + H]$^+$ 292.0290; found 292.0287. Rf 0.2 (Petroleum ether/EtOAc, 5/1).

3,4-dihydroquinolin-2(1H)-one (2l). White solid (10.5 mg, 33%). M.p. = 165-166 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.35 (s, 1H), 7.17 (t, J = 8.9 Hz, 2H), 6.98 (t, J = 7.4 Hz, 1H), 6.86 (d, J = 7.8 Hz, 1H), 2.97 (t, J = 7.6 Hz, 2H), 2.65 (t, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 137.3, 127.9, 127.5, 123.6, 123.1, 115.6, 30.7, 25.3. HRMS (ESI): calcd. for $C_9H_{10}NO$ [M + H]$^+$ 148.0757; found 148.0757.

1-methyl-3,4-dihydroquinolin-2(1H)-one (2m). Yellow oil (20.6 mg, 51%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (ddd, J = 9.0, 7.2, 1.5 Hz, 1H), 7.17 (d, J = 6.7 Hz, 1H), 7.08 – 6.90 (m, 2H), 3.36 (s, 3H), 2.94 – 2.87 (m, 2H), 2.69 – 2.62 (m, 2H).;^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 140.6, 127.7, 127.4, 126.2, 122.8, 114.7, 31.7, 29.5, 25.4. HRMS (ESI): calcd. for C10H12NO [M + H]+ 162.0913; found 162.0915.

1-benzyl-3,4-dihydroquinolin-2(1H)-one (2n). White solid (46.2 mg, 78%). M.p. = 56-57 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (dd, J = 9.9, 5.0 Hz, 2H), 7.22 (dd, J = 12.3, 6.4 Hz, 3H), 7.16 (d, J = 7.3 Hz, 1H), 7.10 (dd, J = 11.2, 4.4 Hz, 1H), 6.99 – 6.93 (m, 1H), 6.86 (d, J = 8.1 Hz, 1H), 5.18 (s, 2H), 3.03 – 2.90 (m, 2H), 2.80-2.77 (m, 2H); ^{13}C

NMR (100 MHz, $CDCl_3$) δ 170.6, 139.9, 137.0, 128.8, 127.8, 127.4, 127.1, 126.4, 122.9, 115.6, 46.2, 31.9, 25.6. HRMS (ESI): calcd. for $C_{16}H_{16}NO$ [M + H]$^+$ 238.1226; found 238.1228.

tert-butyl 4-(2-oxo-3,4-dihydroquinolin-1(2H)-yl)piperidine-1-carboxylate (2o). yellow oil (57.0 mg, 69%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.14 (m, 2H), 7.12-7.10 (m, 1H), 7.03-6.99 (m, 1H), 4.38-4.26 (m, 3H), 2.88 – 2.73 (m, 4H), 2.59-2.51 (m, 4H), 1.73-1.70 (m, 1H), 1.49 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6, 154.7, 140.3, 128.7, 127.8, 127.1, 123.2, 116.5, 79.7, 55.8, 33.6, 28.9, 28.5, 25.8. HRMS (ESI): calcd. for $C_{19}H_{27}N_2O_3$ [M + Na]$^+$ 353.1836; found 353.1835.

1,3-diphenyl-3,4-dihydroquinolin-2(1H)-one (2p). White solid (66.6 mg, 89%). M.p. = 86-87 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (dd, J = 11.5, 4.2 Hz, 2H), 7.39 (t, J = 7.4 Hz, 1H), 7.31 – 7.18 (m, 8H), 7.04 (td, J = 7.6, 1.1 Hz, 1H), 6.98 (dd, J = 10.5, 4.2 Hz, 1H), 6.38 (d, J = 8.0 Hz, 1H), 4.10 – 4.00 (m, 1H), 3.42 – 3.33 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 141.4, 138.7, 138.1, 129.8, 129.0, 128.6, 128.1, 128.1, 127.3, 127.2, 124.8, 123.2, 117.0, 47.2, 33.1. HRMS (ESI): calcd. for $C_{21}H_{18}NO$ [M + H]$^+$ 300.1383; found 300.1383.

1,4-diphenyl-3,4-dihydroquinolin-2(1H)-one (2q). White solid (33.7 mg, 45%). M.p. = 145-146 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (m, 2H), 7.44 – 7.34 (m, 3H), 7.31 – 7.17 (m, 5H), 7.11 – 7.05 (m, 1H), 7.04 – 6.88 (m, 2H), 6.45 (m, 1H), 4.40 (t, J = 6.9 Hz, 1H), 3.24 – 3.06 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 141.5, 141.2, 138.4, 129.9, 129.0, 128.9, 128.6, 128.3, 128.2, 127.8, 127.6, 127.3, 123.3, 117.4, 41.8, 39.4. HRMS (ESI): calcd. for $C_{21}H_{18}NO$ [M + H]$^+$ 300.1383; found 300.1386.

N,N-diphenylcinnamamide (2q'). White solid (33.2 mg, 43%). M.p. = 152-154 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 15.5 Hz, 1H), 7.42 – 7.23 (m, 15H), 6.48 (d, J = 15.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 142.8, 142.6, 135.1, 129.7, 129.3, 128.8, 128.0, 119.8. HRMS (ESI): calcd. for $C_{21}H_{18}NO$ [M + H]$^+$ 300.1383; found 300.1388.

5-phenylphenanthridin-6(5H)-one (2r). White solid (62.3 mg, 92%). M.p. = 227-229 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, J = 7.9 Hz, 1H), 8.48 – 8.16 (m, 2H), 7.84-7.80 (m, 1H), 7.62 (t, J = 7.6 Hz, 3H), 7.54 (t, J = 7.4 Hz, 1H), 7.39 – 7.19 (m, 4H), 6.70 (dd, J = 6.6, 2.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.7, 139.2, 138.3, 134.1, 132.8, 130.2, 129.1, 129.0, 128.8, 128.1, 125.9, 123.0, 122.7, 121.8, 119.0, 117.1. HRMS (ESI): calcd. for $C_{19}H_{14}NO$ [M + H]$^+$ 272.1070; found 272.1076.

5-(4-chlorophenyl)phenanthridin-6(5H)-one (1s). Colorless oil (65.7 mg 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (dd, J = 8.0, 1.1 Hz, 1H), 8.43 – 8.16 (m, 2H), 7.94 – 7.76 (m, 1H), 7.67 – 7.52 (m, 3H), 7.42 – 7.11 (m, 4H), 6.82 – 6.54 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.7, 138.9, 136.7, 134.7, 134.0, 133.0, 130.6, 130.5, 129.2, 129.0, 128.2, 125.6, 123.1, 122.9, 121.8, 119.1, 116.8. HRMS (ESI): calcd. for $C_{19}H_{13}ClNO$ [M + H]$^+$ 306.0680; found 306.0680. Rf 0.2 (Petroleum ether/EtOAc, 5/1).

5-(p-tolyl)phenanthridin-6(5H)-one (1t). Colorless oil (57.6 mg 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (dd, J = 8.0, 1.0 Hz, 1H), 8.43 – 8.27 (m, 2H), 7.84 (ddd, J = 8.3, 7.2, 1.4 Hz, 1H), 7.70 – 7.56 (m, 1H), 7.44 (d, J = 7.9 Hz, 2H), 7.37 – 7.29 (m, 2H), 7.24 (d, J = 8.2 Hz, 2H), 6.81 – 6.71 (m, 1H), 2.51 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.8, 139.3, 138.7, 135.5, 134.0, 132.8, 130.9, 129.0, 128.7, 128.1, 125.9, 122.9, 122.6, 121.7, 119.0, 117.1, 21.3. HRMS (ESI): calcd. for $C_{20}H_{16}NO$ [M + H]$^+$ 286.1226; found 286.1226. Rf 0.2 (Petroleum ether/EtOAc, 5/1).

5-methoxyphenanthridin-6(5H)-one (2u). White solid (26 mg, 47%). M.p. = 95-97 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (dd, J = 8.0, 1.1 Hz, 1H), 8.31 – 8.23 (m, 2H), 7.81 – 7.74 (m, 1H), 7.68 (dd, J = 8.3, 1.0 Hz, 1H), 7.63 – 7.55 (m, 2H), 7.39 – 7.32 (m, 1H), 4.14 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.3, 135.8, 133.0, 132.7, 130.0, 128.5, 128.1, 126.3, 123.2, 122.0, 118.6, 112.6, 62.7. HRMS (ESI): calcd. for $C_{14}H_{12}NO$ [M + H]$^+$ 226.0863; found 226.0859.

5-benzylphenanthridin-6(5H)-one (2v). White solid (61 mg, 85%). M.p. = 128-129 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, J = 7.8 Hz, 1H), 8.27 (t, J = 7.6 Hz, 2H), 7.77 (t, J = 7.5 Hz, 1H), 7.61 (t, J = 7.4 Hz, 1H), 7.42 – 7.34 (m, 1H), 7.30-7.22 (m, 7H), 5.66 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.9, 137.4, 136.6, 133.9, 132.7, 129.6, 129.2, 128.8, 128.1, 127.2, 126.6, 125.5, 123.3, 122.6, 121.7, 119.5, 116.1, 46.5. HRMS (ESI): calcd. for $C_{20}H_{16}NO$ [M + H]$^+$ 286.1226; found 286.1224.

5-methyl-1-phenyl-3,4-dihydroquinolin-2(1H)-one (2w). White solid (30.8 mg, 52%). M.p. = 97-99 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.31 (m, 2H), 7.25-7.22 (m, 3H), 7.10 (d, J = 7.2 Hz, 1H), 7.00 (t, J = 7.4 Hz, 1H), 6.94 (d, J = 7.3 Hz, 1H), 3.02 – 2.93 (m, 2H), 2.78 – 2.69 (m, 2H), 1.59 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 141.2, 140.4, 131.5, 131.1, 129.5, 128.6, 127.2, 126.2, 125.1, 124.5, 33.9, 26.6, 20.5. HRMS (ESI): calcd. for $C_{16}H_{16}NO$ [M + H]$^+$ 238.1226; found 238.1226.

6-bromo-1-phenyl-3,4-dihydroquinolin-2(1H)-one (2x). White solid (37 mg, 49%). M.p. = 90-92 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (t, J = 7.6 Hz, 2H), 7.45 (t, J = 7.4 Hz, 1H), 7.21 (d, J = 7.4 Hz, 2H), 7.11 (dd, J = 8.0, 1.6 Hz, 1H), 7.07 (d, J = 8.0 Hz, 1H). 6.48 (d, J = 1.4 Hz, 1H), 3.05 – 2.99 (m, 2H), 2.85 – 2.79 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 143.0, 137.8, 130.1, 129.1, 128.9, 128.6, 125.8, 124.5, 120.6, 119.9, 32.0, 25.3. HRMS (ESI): calcd. for $C_{15}H_{13}BrNO$ [M + H]$^+$ 302.0175; found 302.0175.

6-methyl-1-phenyl-3,4-dihydroquinolin-2(1H)-one (2y). White solid (38 mg, 63%). M.p. = 107-109 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.49 (m, 2H), 7.44-7.41 (m, 1H), 7.28 – 7.20 (m, 2H), 7.10-7.08 (d, J = 7.5 Hz, 1H), 6.80 (d, J = 7.4 Hz, 1H), 6.16 (s, 1H), 3.02 (t, J = 7.2 Hz, 2H), 2.80 (t, J = 7.2 Hz, 2H), 2.15 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 141.6, 138.5, 137.0, 129.8, 129.1, 128.2, 127.6, 123.6, 122.7, 117.7, 32.5, 25.3, 21.3.HRMS (ESI): calcd. for $C_{16}H_{16}NO$ [M + H]$^+$ 238.1226; found 238.1231.

8-methyl-1-phenyl-3,4-dihydroquinolin-2(1H)-one (2y'). Colourless oil (11 mg, 18%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (t, J = 7.5 Hz, 2H), 7.41 (t, J = 7.1 Hz, 1H), 7.22 (d, J = 7.6 Hz, 2H), 6.93 (t, J = 7.8 Hz, 1H), 6.87 (d, J = 7.4 Hz, 1H), 6.21 (d, J = 7.9 Hz, 1H), 3.02 (t, J = 7.3 Hz, 2H), 2.81 (t, J = 7.3 Hz, 2H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 141.8, 138.8, 135.6, 129.8, 129.1, 128.1, 126.6, 124.9, 124.3, 115.3, 31.8, 21.9, 19.6. HRMS (ESI): calcd. for $C_{16}H_{16}NO$ [M + H]$^+$ 238.1226; found 238.1227.

1-phenyl-1-azaspiro[4.5]deca-6,9-diene-2,8-dione (2aa). White solid (52 mg, 87%). M.p. = 148-150 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.22 (m, 3H), 7.17 (d, J = 7.4 Hz, 2H), 6.99 (d, J = 10.1 Hz, 2H), 6.26 (d, J = 10.0 Hz, 2H), 2.78 (t, J = 8.0 Hz, 2H), 2.33 (t, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.3, 174.0, 149.8, 136.3, 129.8, 129.2, 127.8, 126.1, 63.9, 31.7, 29.8. HRMS (ESI): calcd. for $C_{15}H_{14}NO_2$ [M + H]$^+$ 240.1019; found 240.1021.

1-benzyl-1-azaspiro[4.5]deca-6,9-diene-2,8-dione (2ab). Yellow oil (52.6 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, J = 4.0 Hz, 3H), 7.20 – 7.12 (m, 2H), 6.56 (d, J = 9.9 Hz, 2H), 6.16 (d, J = 9.9 Hz, 2H), 4.32 (s, 2H), 2.66 (t, J = 8.1 Hz, 2H), 2.15 (t, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.5, 174.6, 149.2, 137.5, 129.7, 128.7, 128.5, 127.8, 62.3, 44.8, 30.3, 29.2. HRMS (ESI): calcd. for $C_{16}H_{16}NO_2$ [M + H]$^+$ 254.1176; found 254.1179.

1-phenyl-1-azaspiro[4.5]deca-7,9-diene-2,6-dione (2ac). White solid (42.9 mg, 80%). M.p. = 123-124 °C. ^{1}H NMR (400 MHz, CDCl3) δ 7.32 – 7.25 (m, 2H), 7.20 – 7.02 (m, 4H), 6.38 (dd, J = 9.5, 1.0 Hz, 1H), 6.31 – 6.27 (m, 1H), 6.21 (d, J = 9.8 Hz, 1H), 2.91 – 2.82 (m, 1H), 2.62 – 2.55 (m, 1H), 2.33 – 2.27 (m, 1H), 2.14 – 2.05 (m, 1H); ^{13}C

NMR (100 MHz, CDCl3) δ 199.9, 174.9, 143.7, 141.7, 137.2, 128.9, 126.2, 125.3, 123.6, 123.2, 72.2, 29.3, 28.4. HRMS (ESI): calcd. for $C_{15}H_{14}NO_2$ $[M + H]^+$ 240.1019; found 240.1022.

1-benzyl-1-azaspiro[4.5]deca-7,9-diene-2,6-dione (2ad). Yellow oil (50.0 mg, 79%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.16 (m, 3H), 6.95 – 6.90 (m, 1H), 6.10 – 5.95 (m, 2H), 4.65 (d, J = 14.8 Hz, 1H), 3.96 (d, J = 14.8 Hz, 1H), 2.77 – 2.67 (m, 1H), 2.53 – 2.45 (m, 1H), 2.19 – 2.11 (m, 1H), 1.94 – 1.85 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.8, 176.2, 143.1, 141.0, 136.8, 129.1, 128.3, 127.7, 125.2, 122.5, 70.7, 45.9, 29.4, 28.0. HRMS (ESI): calcd. for $C_{16}H_{16}NO_2$ $[M + H]^+$ 254.1176; found 254.1181.

phenanthridin-6(5H)-one (3)[11b]**.** White solid (42.8 mg, 87%). White solid,^1H NMR (300 MHz; DMSO) δ 11.70 (s, 1H), 8.51 (d, J = 8.1 Hz, 1H), 8.45−8.25 (m, 2H), 7.91−7.82 (m, 1H), 7.78−7.65 (m, 1H), 7.53-7.46 (m, 1H), 7.43-7.36 (m, 1H), 7.32-7.18 (m, 1H); ^{13}C NMR (75 MHz; DMSO) δ 161.3, 137.0, 134.7, 133.3, 130.0, 128.4, 127.9, 126.2, 123.7, 123.0, 122.7, 118.0, 116.6.

Conflicts of interest

There are no conflicts to declare.

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10 CCDC 1906915 (2w) contains supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre.

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