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Free radical cyclization reactions of allylsulfonyl substituted *N*-aryl amide derivatives

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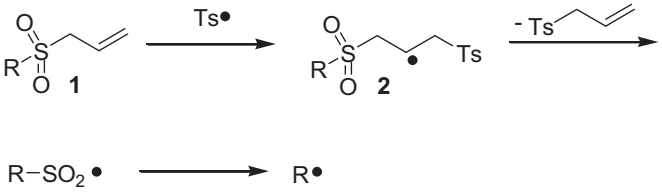
ABSTRACT

p-Toluenesulfonyl radical can be generated by the manganese(III) acetate oxidation of sodium *p*-toluenesulfinate. The corresponding alkyl radicals could be produced effectively by the *p*-toluenesulfonyl radical induced radical reaction of allylsulfonyl substituted *N*-aryl amides. These alkyl radicals undergo 5-*exo*-*trig*, 6-*endo*-*trig*, or 6-*exo*-*trig* cyclization onto the aromatic ring effectively. The product distribution is highly dependent on the substituent of aromatic ring and the stability of radical intermediate. This *p*-toluenesulfonyl radical induced reaction provides a synthetically useful method for the synthesis of dihydroquinolinones, azaspirocyclic cyclohexadienes, and spirodihydroquinolinones.

1. Introduction

Free radical reactions have received considerable attention during the last two decades and there is a tremendous development of new radical reactions designed for organic synthesis.[1,2] Free radical reactions mediated by sulfonyl radicals have been noted by several groups.[3–5] The α-scission of most alkylsulfonyl radicals to generate alkyl radicals is an unfavorable process, but if the alkyl group represents a stabilized radical, the extrusion of sulfur dioxide occurs readily.[6] *p*-Toluenesulfonyl radical can be generated by the Mn(III) oxidation of sodium *p*-toluenesulfinate.[7] The alkyl radicals generated from *p*-toluenesulfonyl radical induced reaction of allylsulfones (Scheme 1) can undergo free radical cyclization reactions effectively.[5c,d]

Quinolinones have long been targeted in synthetic investigations for their known biological activities and pharmacological properties, which include antiviral (HIV) activities,[8a–c] inotropic,[8d] $5HT_3$ receptor antagonists,[8e] farnesyl transferase inhibitors,[8f] and maxi-K channel opening agents.[8g] The development of new and efficient method for their synthesis represents a challenge in organic and medical chemistry. Alongside classical Friedlander/Friedel–Crafts cyclization approaches,[9] more recent methods have been employed in the synthesis of quinolinones including oxidative cyclization of 2-(3-hydroxypropyl) anilines,[10] radical cyclization of anilides,[11] palladium-catalyzed cyclocarbonylation of 2-alkenylanilines,[12] rhodium catalyzed addition-cyclization of aminophenylboronates.[13] This report describes our results on the free radical cyclization reactions of allylsulfonyl substituted *N*-aryl amide derivatives mediated by sodium *p*-toluenesulfinate/manganese(III) acetate.



Scheme 1.

2. Results and discussion

Our studies commenced with the readily available β-allylsulfonylpropanamide **5a** (R=Me, PG=Et, E=CO_2Et), which was prepared by the alkylation of 2-bromo-*N*-ethyl-*N*-(4-methylphenyl)-ethanamide with ethyl allylsulfonylacetate (see Supplementary data). With this propanamide **5a** in hand, we examined the reaction of **5a**

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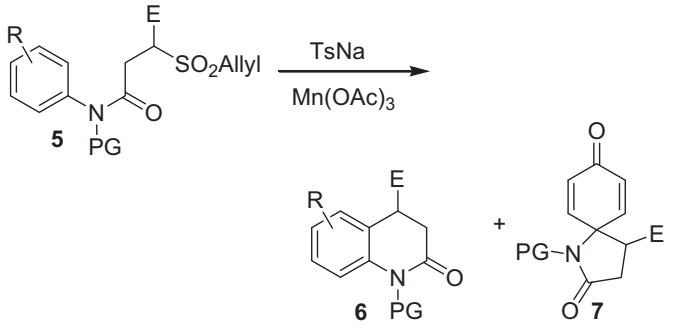
with sodium *p*-toluenesulfinate/manganese(III) acetate under various reaction conditions (Scheme 2). When the reaction of **5a** with sodium *p*-toluenesulfinate and manganese(III) acetate was carried out in CF_3CH_2OH at room temperature, the expected dihydroquinolinone **6a** was obtained in 89% yield (Table 1, entry 1). Encouraged by this preliminary result, different solvents including acetonitrile, methanol, DME, and DMSO were screened by using **5a** as substrate. As shown in Table 1, it was found that the best result was accessed in CF_3CH_2OH (entry 1). In acetonitrile, **6a** was obtained in good yield (90%), however, it proceeded sluggishly and it needs 4 h to complete the reaction (entry 2). When the reactions were performed in methanol, DME, and DMSO, the desired product **6a** was produced in lower yields (entries 3–5).



Scheme 2.

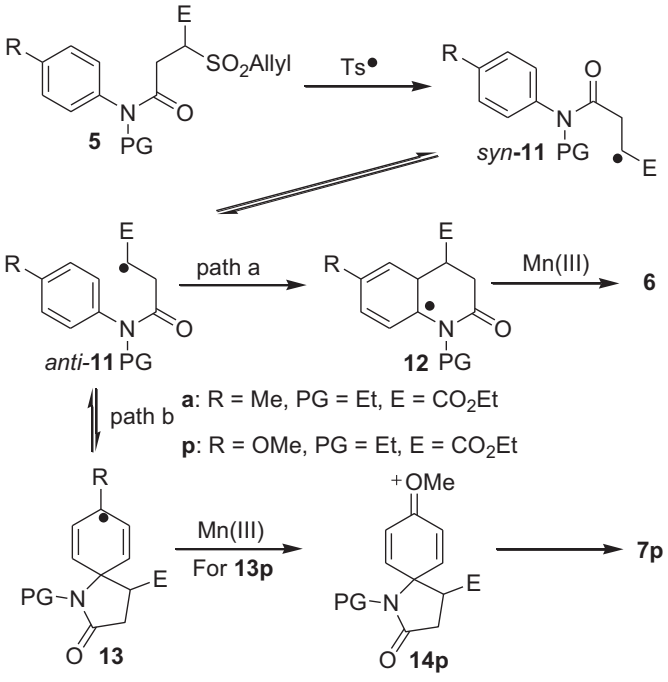
Table 1
Optimization of reaction conditions

Entry	Solvent	Reaction time	Product (yield (%))
1	CF_3CH_2OH	45 min	**6a**(89)
2	CH_3CN	4 h	**6a**(90)
3	CH_3OH	2 h	**6a**(64)
4	DME	2 h	**6a**(49)
5	DMSO	30 min	**6a**(55)

This dihydroquinolinone **6a** was formed by the reaction mechanism outlined in Scheme 3. Radical **11a** (R=Me, PG=Et, E=CO_2Et) generated from **5a** via a similar reaction route shown in Scheme 1 undergoes a 6-*endo*-*trig* ring cyclization (path a) to produce radical intermediate **12a**, which is subsequently oxidized by manganese(III) acetate to give dihydroquinolinone **6a** via deprotonation and aromatization. The 5-*exo*-*trig* (*ipso*-type)[14] cyclization of radical **11a** (path b) may also occur to afford the cyclohexadienyl radical intermediate **13a**. This radical intermediate **13a** is extremely unstable and would undergo fragmentation back to radical **11a**. Therefore, no product derived from 5-*exo*-*trig* cyclization of radical **11a** was observed.

The scope of this transformation was next investigated according to the optimized reaction conditions (Table 1, entry 1). As shown in Table 2, a great variety of β-allylsulfonylpropanamides **5a**–**m** were converted to the corresponding dihydroquinolinones **6a**–**m** effectively. In all cases, β-allylsulfonylpropanamides **5a**–**m** bearing a radical stabilizing substituent (E) underwent this radical reaction in excellent to good yields. This process was well tolerant toward a variety of arylic substituents (R). However, an electron-donating substituent favored product formation (entries 1–5), whereas an electron-withdrawing substituent slightly hindered the reaction (entries 8–13).

When *N*-4-methoxyphenyl substituted propanamide **5p** (R=OMe, PG=Et, E=CO_2Et) was treated with sodium *p*-toluenesulfinate and manganese(III) acetate in CF_3CH_2OH, in addition to the



Scheme 3.

Table 2
Reactions of β-allylsulfonylpropanamides **5a**–**m**[a]

Entry	Amide	R	E	Product (yield (%))
1	**5a**	4-Me	CO_2Et	**6a**(89)
2	**5b**	4-Me	*p*-ClC_6H_4CO	**6b**(86)
3	**5c**	4-Me	CH_3CO	**6c**(95)
4	**5d**	3,5-diMe	CO_2Et	**6d**(98)
5	**5e**	3,5-diMe	*p*-ClC_6H_4CO	**6e**(92)
6	**5f**	—	*p*-ClC_6H_4CO	**6f**(87)
7	**5g**	—	CH_3CO	**6g**(89)
8	**5h**	4-Cl	*p*-ClC_6H_4CO	**6h**(80)
9	**5i**	4-Cl	CH_3CO	**6i**(81)
10	**5j**	4-Br	*p*-ClC_6H_4CO	**6j**(76)
11	**5k**	4-Br	CH_3CO	**6k**(83)
12	**5l**	4-CO_2Et	CO_2Et	**6l**(64)
13	**5m**	4-CO_2Et	*p*-ClC_6H_4CO	**6m**(74)

[a] PG=Et.

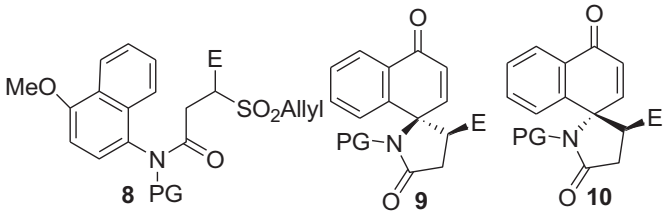
expected dihydroquinolinone **6p** (68%), a spirolactam **7p** was also produced in 31% yield (Table 3, entry 3). This spirolactam **7p** was formed via the reaction route outlined in Scheme 3 (path b).[15] Radical **11p** generated from **5p** undergoes 5-*exo*-*trig* cyclization to afford cyclohexadienyl radical intermediate **13p**, which is then

Table 3
Reactions of *N*-4-methoxyphenyl substituted propanamides[a]

Entry	Amide	E	PG	Product (yield (%))	
1	**5n**	*p*-ClC_6H_4CO	Et	**6n**(86)	**7n**(0)
2	**5o**	CH_3CO	Et	**6o**(89)	**7o**(0)
3	**5p**	CO_2Et	Et	**6p**(68)	**7p**(31)
4	**5q**	$PhSO_2$	Et	**6q**(16)	**7q**(64)
5	**5r**	H	Et	**6r**(0)	**7r**(47)
6	**5s**	Me	Et	**6s**(0)	**7s**(65)
7	**5t**	H	TMBn[b]	**6t**(0)	**7t**(54)
8	**5u**	Me	TMBn[b]	**6u**(0)	**7u**(76)
9	**5v**	$PhSO_2$	TMBn[b]	**6v**(0)	**7v**(81)
10	**8a**	$PhSO_2$	Et	**9a**(70)	**10a**(24)
11	**8b**	CO_2Et	Et	**9b**(46)	**10b**(40)
12	**8c**	H	Et	**9c**(62)	

[a] R=OMe.
[b] TMBn=2,4,6-Trimethylbenzyl.

oxidized by manganese(III) acetate to give oxonium ion **14p**. This oxonium ion **14p** would then be transformed into the observed spirolactam **7p** by the attack of the solvent or water. In contrast to the selective formation of **6a**–**m** shown in Table 2, spirolactam **7p** was also formed from **5p**. This is likely to be attributed to the ionization potential of cyclohexadienyl radical **13p** having a 4-methoxy group must be lower than that of other cyclohexadienyl radicals **13a**–**m**. Therefore once radical **11p** undergoes 5-*exo* cyclization to produce the corresponding cyclohexadienyl radical **13p**, which could be immediately subjected to irreversible oxidation by manganese(III) acetate followed by demethylation to give spirolactam **7p**. In order to scrutinize the effect of β-substituent (E) on the regioselectivity for this radical cyclization reaction, we examined the radical reaction of *N*-(4-methoxyphenyl)-propanamides **5n**–**s**. As shown in Table 3, the **6**/**7** ratio is highly dependent on the stability of radical intermediate **11**. In particular, with **5n** and **5o** bearing a strong electron-withdrawing substituent, dihydroquinolinones **6n** and **6o** were produced exclusively (entries 1 and 2). On the contrary, with **5r** and **5s**, spirolactams **7r** and **7s** are the only products (entries 5 and 6). Presumably, due to the strong electron-withdrawing keto groups, the fragmentation of cyclohexadienyl radical intermediates **13n** and **13o** back to the stable radicals **11n** and **11o** proceeded much faster than the manganese(III) oxidation to produce oxonium ions **14n** and **14o**. On the other hand, the fragmentation of cyclohexadienyl radical intermediates **13r** and **13s** to produce the less stable radicals **11r** and **11s** proceeded much slower and the manganese(III) oxidation of **13r** and **13s** to generate oxonium ions **14r** and **14s** became the only route. With **5q** bearing a benzenesulfonyl group, spirolactam **7q** is the major product (entry 4) and the **7**/**6** ratio could be increased by changing the ethyl group (PG) with the bulkier 2,4,6-trimethylbenzyl group (entry 9).[16] Owing to the generation of the less stable primary and secondary alkyl radicals by the sulfur dioxide extrusion of alkylsulfonyl radicals is a less favorable process, the radical cyclizations of **5r** and **5s** are less productive (entries 5 and 6). The yields of spiro derivatives could be improved by replacing the ethyl group (PG) with the bulkier 2,4,6-trimethylbenzyl group (entries 7 and 8). This can be reasoned that the introduction of a large PG group would shift the equilibrium in favor of the *anti*-**11** conformer, which then could cyclize (Scheme 3).[17] We also conducted this reaction with the naphthalene precursors **8a** and **8b** (entries 10 and 11). The reaction worked well, and spirolactams **9a**,**b** and their stereoisomers **10a**,**b** were formed exclusively in excellent yields (Scheme 4). The stereochemistry of **9a** was confirmed by single crystal X-ray analysis (Fig. 1).[18] Similarly, spirolactam **9c** was formed as the only product from **8c** in 62% yield (entry 12).



Scheme 4.

Spirodihydroquinolinone **15** is the key intermediate in the preparation of aza-galanthamine[19] and other indole alkaloids.[20] Methods that have been employed for their syntheses are less abundant, which include palladium-catalyzed Heck cyclization of 2-cyclohexenylacetanilides,[20] oxidative cyclization of 2-(*p*-hydroxyphenyl)-acetanilides,[21] and radical cyclization of 2-(*p*-alkoxy or *p*-azido substituted phenyl)-acetanilides.[15b,e] The development of efficient methods for their synthesis remains an area of current interest. In view of the results on the spirolactam

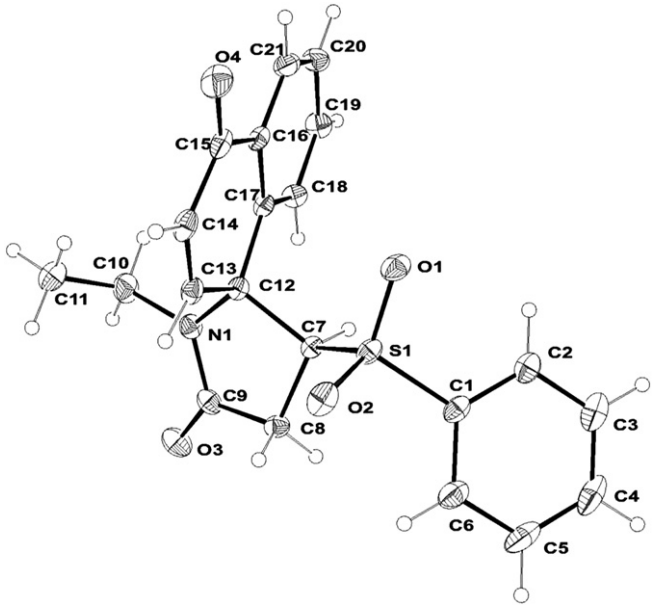
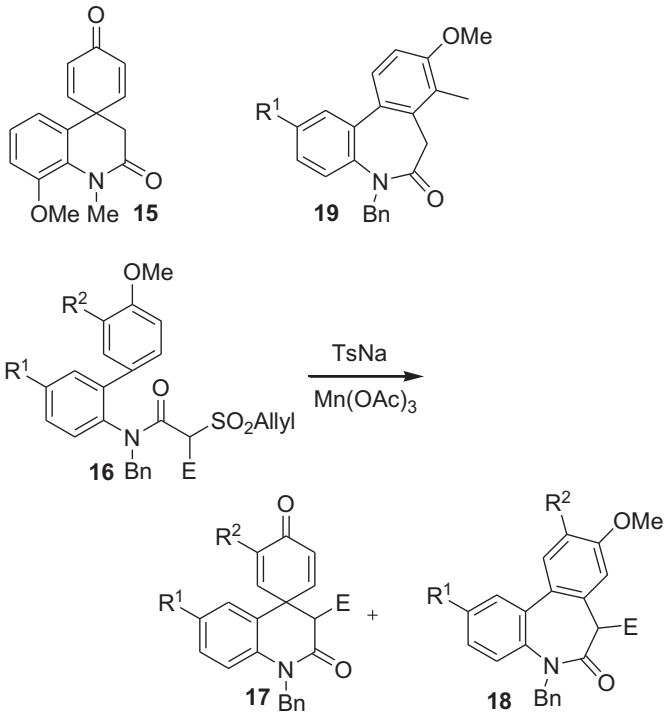


Fig. 1. The molecular structure of **9a**.

formation shown in Table 3, we reasoned that it might be possible to form spirodihydroquinolinone derivatives **17** through the sodium *p*-toluenesulfinate/manganese(III) acetate mediated radical reaction of α-(allylsulfonyl)-*N*-(4′-methoxybiphen-2-yl)-ethanamides **16** (Scheme 5).



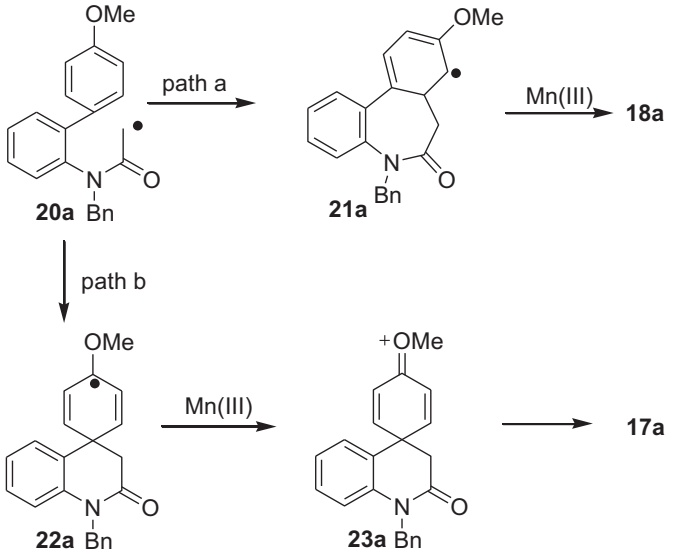
Scheme 5.

Indeed, ethanamide **16a** (R^1=R^2=E=H) was transformed into the desired spirodihydroquinolinone **17a** (75%) by the reaction of **16a** with sodium *p*-toluenesulfinate and manganese(III) acetate in CF_3CH_2OH at room temperature (Table 4, entry 1). A possible reaction mechanism for the formation of spirodihydroquinolinone **17a** is shown in Scheme 6. Radical **20a** generated from **16a**

Table 4
Reactions of *N*-(4′-methoxybiphen-2-yl) substituted ethanamides **16**

Entry	Amide	R^1	R^2	E	Product (yield (%))	
1	**16a**	H	H	H	**17a**(75)	**18a**(9)
2	**16b**	Me	H	H	**17b**(76)	**18b**(14)
3	**16c**	Cl	H	H	**17c**(72)	**18c**(12)
4	**16d**	H	Me	H	**17d**(82)	**18d**(5)
5	**16e**	Me	Me	H	**17e**(83)	**18e**(6)
6	**16f**	Cl	Me	H	**17f**(82)	**18f**(6)
7	**16g**	H	H	Me	**17g**(95)	**18a**(0)
8	**16h**	Me	H	Me	**17h**(96)	**18a**(0)
9	**16i**	Cl	H	Me	**17i**(94)	**18a**(0)

undergoes a 6-*exo* cyclization (path b) to afford cyclohexadienyl radical **22a**, which is then oxidized by manganese(III) acetate to give oxonium ion **23a**. This oxonium ion **23a** would then be attacked by the solvent or water to produce spirolactam **17a**. In addition to spirodihydroquinolinone **17a**, a small amount (9%) of dibenzoazepinone **18a** formed by 7-*exo* cyclization of radical **20a** (path a) was also obtained. It is noteworthy to note that no products derived from the five- or six-membered ring cyclization of radical **20a** onto the other two benzene rings can be observed.



Scheme 6.

To investigate the scope of this spirolactamization process, a series of **16** was prepared and subjected to the optimized reaction conditions shown in Table 1 (entry 1). As shown in Table 4, a great variety of *N*-(4′-methoxybiphen-2-yl) substituted amides **16** were converted to the corresponding spirodihydroquinolinones **17** effectively. The expected spirodihydroquinolinones **17** were formed predominantly and a small amount of dibenzoazepinones **18** was also obtained. With ethanamides **16d**–**f**, the steric hindrance of the methyl group (R^2) might contribute to the exclusive production of dibenzoazepinones **18d**–**f** and their isomeric products **19d**–**f** cannot be found (entries 4–6). Secondary allylsulfones **16g**–**i** can also be used, in which cases spirodihydroquinolinones **17g**–**i** containing a methyl substituent (E) α to the lactam carbonyl group are produced in better reaction yields (entries 7–9).

3. Conclusions

p-Toluenesulfonyl radical can be generated by the manganese(III) acetate oxidation of sodium *p*-toluenesulfinate. This *p*-toluenesulfonyl radical can induce the free radical reaction of allylsulfonyl substituted *N*-aryl amides and the corresponding alkyl radicals can be generated efficiently. These alkyl radicals undergo 5-*exo*-*trig*, 6-*endo*-*trig*, or 6-*exo*-*trig* cyclization onto the aromatic ring effectively. With β-allylsulfonylpropanamides **5**, this reaction provides a synthetically useful method for the synthesis of dihydroquinolinones and azaspirocyclic cyclohexadienes. The product distributions are highly dependent on the substituent of aromatic ring and the stability of radical intermediate **11**. With α-allylsulfonylethanamides **16**, spirodihydroquinolinones **17** were obtained as the exclusive or major products.

4. Experimental section

4.1. General

Melting points are uncorrected. The NMR spectra were recorded on a Brucker AMX-400 or AVANCE 500 spectrometer. Chemical shifts are reported in parts per million relative to TMS as internal reference. Elemental analyses were performed with Heraeus CHN-Rapid Analyzer. HRMS were recorded on a JEOL JMS-SX 102A mass spectrometer. X-ray diffraction structure analyses were performed with a Nonius Kappa CCD diffractometer. Structure analysis was made by using SHELXTL program on a personal computer. Analytical thin-layer chromatography was performed with precoated silica gel 60 F_{254} plates (0.25 mm thick) and visualized by UV light. The reaction mixture was purified by column chromatography over silica gel (70–230 mesh).

Typical procedure for the radical reaction: A mixture of 128 mg (0.35 mmol) of **5a**, 233 mg (0.87 mmol) of manganese(III) acetate, and 373 mg (2.1 mmol) of sodium *p*-toluenesulfinate in 10 mL of CF_3CH_2OH was stirred at room temperature for 45 min. The reaction mixture was diluted with 100 mL of EtOAc, washed with saturated aqueous bisulfite (2×50 mL), H_2O (3×50 mL), dried (Na_2SO_4), and concentrated in vacuo. The residue was chromatographed over 20 g of silica gel (eluted with 8:1 hexane–EtOAc) followed by recrystallization (hexane–EtOAc) to give 81 mg (89%) of **6a**.

*4.1.1. 4-Ethoxycarbonyl-1-ethyl-6-methyl-3,4-dihydro-2(1H)-quinolinone **6a**.* White needles; mp 72–73 °C; IR ($CHCl_3$) 2920, 1730, 1665, 1615, 1590, 1505 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.15–1.30 (m, 6H, CH_3), 2.31 (s, 3H, CH_3), 2.76 (dd, *J*=16.0, 6.2 Hz, 1H, CH), 2.96 (dd, *J*=16.0, 4.4 Hz, 1H, CH), 3.77 (dd, *J*=6.2, 4.4 Hz, 1H, CH), 3.88–4.07 (m, 2H, NCH_2), 4.07–4.21 (m, 2H, OCH_2), 6.93 (d, *J*=8.3 Hz, 1H, ArH), 7.07 (s, 1H, ArH), 7.10 (d, *J*=8.3 Hz, 1H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 12.5 (q), 14.0 (q), 20.5 (q), 34.0 (t), 37.0 (t), 42.4 (d), 61.3 (t), 115.0 (d), 122.9 (s), 129.2 (d), 129.3 (d), 132.4 (s), 136.7 (s), 167.4 (s), 171.6 (s); Anal. Calcd for $C_{15}H_{19}NO_3$: C, 68.94; H, 7.33; N 5.36. Found: C, 68.70; H, 7.29; N, 5.33.

*4.1.2. 4-(4-Chlorobenzoyl)-1-ethyl-6-methyl-3,4-dihydro-2(1H)-quinolinone **6b**.* White crystals; mp 138–139 °C; IR ($CHCl_3$) 3015, 1680, 1660, 1385, 1175 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.26 (t, *J*=7.1 Hz, 3H, CH_3), 2.21 (s, 3H, CH_3), 2.83 (dd, *J*=15.9, 6.1 Hz, 1H, CH), 2.98 (dd, *J*=15.9, 6.1 Hz, 1H, CH), 3.91–4.07 (m, 2H, NCH_2), 4.77 (t, *J*=6.1 Hz, 1H, CH), 6.84 (s, 1H, ArH), 6.96 (d, *J*=8.3 Hz, 1H, ArH), 7.07 (d, *J*=8.3 Hz, 1H, ArH), 7.47 (d, *J*=8.6 Hz, 2H, ArH), 7.95 (d, *J*=8.6 Hz, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 12.5 (q), 20.5 (q), 34.5 (t), 37.2 (t), 43.1 (d), 115.3 (d), 123.6 (s), 128.9 (d), 129.1 (d), 129.2 (2× d), 130.1 (2× d), 132.4 (s), 134.2 (s), 137.4 (s), 140.1 (s), 167.8 (s), 197.2 (s); Anal. Calcd for $C_{19}H_{18}ClNO_2$: C, 69.62; H, 5.53; N, 4.27. Found: C, 69.34; H, 5.60; N, 4.23.

*4.1.3. 4-Acetyl-1-ethyl-6-methyl-3,4-dihydro-2(1H)-quinolinone **6c**.* White needles; mp 103–104 °C; IR ($CHCl_3$) 3010, 1715, 1665, 1380, 1135 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.20 (t, *J*=7.1 Hz, 3H, CH_3), 2.16 (s, 3H, CH_3), 2.34 (s, 3H, CH_3), 2.68 (dd, *J*=16.0, 6.2 Hz, 1H, CH),

2.99 (dd, J=16.0, 2.8 Hz, 1H, CH), 3.74 (dd, J=6.2, 2.8 Hz, 1H, CH), 3.94 (q, J=7.1 Hz, 2H, NCH_2), 6.94 (d, J=8.7 Hz, 1H, ArH), 7.10 (s, 1H, ArH), 7.11 (d, J=8.7 Hz, 1H, ArH); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 12.4 (q), 20.5 (q), 27.6 (q), 33.2 (t), 37.0 (t), 50.0 (d), 115.2 (d), 122.9 (s), 129.3 (d), 129.8 (d), 132.6 (s), 136.9 (s), 167.8 (s), 205.4 (s); Anal. Calcd for $C_{14}H_{17}NO_2$: C, 72.70; H, 7.41; N, 6.06. Found: C, 72.54; H, 7.44; N, 6.06.

4.1.4. 4-Ethoxycarbonyl-1-ethyl-5,7-dimethyl-3,4-dihydro-2(1H)-quinolinone ***6d***. White crystals; mp 71–72 °C; IR ($CHCl_3$) 2980, 1725, 1660, 1320, 1275 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.19 (t, J=7.2 Hz, 3H, CH_3), 1.22 (t, J=7.3 Hz, 3H, CH_3), 2.33 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 2.68 (dd, J=16.0, 6.5 Hz, 1H, CH), 2.99 (dd, J=16.0, 1.4 Hz, 1H, CH), 3.94 (dd, J=6.5, 1.4 Hz, 1H, CH), 3.98 (q, J=7.2 Hz, 2H, NCH_2), 4.03–4.15 (m, 2H, OCH_2), 6.73 (s, 1H, ArH), 6.75 (s, 1H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 12.7 (q), 14.0 (q), 19.6 (q), 21.5 (q), 34.1 (t), 37.4 (t), 38.5 (d), 61.2 (t), 114.1 (d), 119.2 (s), 126.0 (d), 136.9 (s), 138.2 (s), 139.5 (s), 167.7 (s), 171.6 (s); Anal. Calcd for $C_{16}H_{21}NO_3$: C, 69.79; H, 7.69; N, 5.09. Found: C, 69.60; H, 7.75; N, 5.08.

4.1.5. 4-(4-Chlorobenzoyl)-1-ethyl-5,7-dimethyl-3,4-dihydro-2(1H)-quinolinone ***6e***. White crystals; mp 199–200 °C; IR ($CHCl_3$) 3010, 1685, 1660, 1380, 1140 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.27 (t, J=7.1 Hz, 3H, CH_3), 2.14 (s, 3H, CH_3), 2.35 (s, 3H, CH_3), 2.91 (dd, J=16.0, 2.0 Hz, 1H, CH), 3.00 (dd, J=16.0, 7.7 Hz, 1H, CH), 4.00 (q, J=7.1 Hz, 2H, NCH_2), 4.86 (dd, J=7.7, 2.0 Hz, 1H, CH), 6.73 (s, 1H, ArH), 6.81 (s, 1H, ArH), 7.47 (d, J=8.6 Hz, 2H, ArH), 7.90 (d, J=8.6 Hz, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 12.6 (q), 19.7 (q), 21.5 (q), 34.9 (t), 37.5 (t), 40.5 (d), 114.4 (d), 119.7 (s), 125.9 (d), 129.2 (2× d), 129.8 (2× d), 133.7 (s), 135.5 (s), 138.3 (s), 140.0 (s), 140.4 (s), 166.3 (s), 197.0 (s); Anal. Calcd for $C_{20}H_{20}ClNO_2$: C, 70.27; H, 5.90; N, 4.10. Found: C, 70.27; H, 5.99; N, 4.08.

4.1.6. 4-(4-Chlorobenzoyl)-1-ethyl-3,4-dihydro-2(1H)-quinolinone ***6f***. White needles; mp 109–110 °C; IR ($CHCl_3$) 2925, 1685, 1665, 1385, 1260 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.28 (t, J=7.1 Hz, 3H, CH_3), 2.85 (dd, J=15.9, 6.1 Hz, 1H, CH), 3.01 (dd, J=15.9, 6.1 Hz, 1H, CH), 3.96–4.10 (m, 2H, NCH_2), 4.80 (t, J=6.1 Hz, 1H, CH), 6.94 (t, J=7.7 Hz, 1H, ArH), 7.04 (d, J=7.7 Hz, 1H, ArH), 7.07 (d, J=7.7 Hz, 1H, ArH), 7.27 (t, J=7.7 Hz, 1H, ArH), 7.47 (d, J=8.6 Hz, 2H, ArH), 7.94 (d, J=8.6 Hz, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 12.6 (q), 34.3 (t), 37.3 (t), 43.2 (d), 115.4 (d), 122.8 (d), 123.7 (s), 128.3 (d), 128.7 (d), 129.2 (2× d), 130.1 (2× d), 134.3 (s), 139.9 (s), 140.2 (s), 167.9 (s), 197.0 (s); Anal. Calcd for $C_{18}H_{16}ClNO_2$: C, 68.90; H, 5.14; N, 4.46. Found: C, 68.93; H, 5.15; N, 4.47.

4.1.7. 4-Acetyl-1-ethyl-3,4-dihydro-2(1H)-quinolinone ***6g***. White needles; mp 99–100 °C; IR ($CHCl_3$) 3015, 1715, 1670, 1385, 1135 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.21 (t, J=7.1 Hz, 3H, CH_3), 2.16 (s, 3H, CH_3), 2.70 (dd, J=16.1, 6.1 Hz, 1H, CH), 3.01 (dd, J=16.1, 2.7 Hz, 1H, CH), 3.80 (dd, J=6.1, 2.7 Hz, 1H, CH), 3.87–4.04 (m, 2H, NCH_2), 7.02–7.10 (m, 2H, ArH), 7.28–7.34 (m, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 12.5 (q), 27.6 (q), 33.1 (t), 37.1 (t), 49.9 (d), 115.3 (d), 122.9 (d), 128.9 (d), 129.2 (d), 139.4 (s), 167.9 (s), 205.2 (s); Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.87; H, 6.96; N, 6.45. Found: C, 71.86; H, 7.04; N, 6.41.

4.1.8. 6-Chloro-4-(4-chlorobenzoyl)-1-ethyl-3,4-dihydro-2(1H)-quinolinone ***6h***. White crystals; mp 145–146 °C; IR ($CHCl_3$) 3015, 1680, 1670, 1380, 1135 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.26 (t, J=7.1 Hz, 3H, CH_3), 2.86 (dd, J=16.0, 5.9 Hz, 1H, CH), 2.99 (dd, J=16.0, 5.9 Hz, 1H, CH), 3.91–4.08 (m, 2H, NCH_2), 4.77 (t, J=5.9 Hz, 1H, CH), 6.99 (d, J=8.8 Hz, 1H, ArH), 7.03 (d, J=2.4 Hz, 1H, ArH), 7.24 (dd, J=8.8, 2.4 Hz, 1H, ArH), 7.50 (d, J=8.6 Hz, 2H, ArH), 7.93 (d, J=8.6 Hz, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 12.4 (q), 34.2 (t), 37.4 (t), 42.9 (d), 116.6 (d), 125.3 (s), 127.9 (s), 128.3 (d), 128.6 (d), 129.4 (2× d), 130.0 (2× d), 133.7 (s), 138.6 (s), 140.6 (s), 167.4 (s), 196.4 (s); Anal. Calcd for $C_{18}H_{15}Cl_2NO_2$: C, 62.08; H, 4.34; N, 4.02. Found: C, 62.05; H, 4.36; N, 4.06.

4.1.9. 4-Acetyl-6-chloro-1-ethyl-3,4-dihydro-2(1H)-quinolinone ***6i***. White crystals; mp 132–133 °C; IR ($CHCl_3$) 3015, 1715, 1675, 1375, 1135 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.19 (t, J=7.1 Hz, 3H, CH_3), 2.19 (s, 3H, CH_3), 2.69 (dd, J=16.1, 6.1 Hz, 1H, CH), 3.01 (dd, J=16.1, 2.6 Hz, 1H, CH), 3.77 (dd, J=6.1, 2.6 Hz, 1H, CH), 3.87–3.99 (m, 2H, NCH_2), 6.95–6.99 (m, 1H, ArH), 7.26–7.31 (m, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 12.3 (q), 27.7 (q), 32.9 (t), 37.2 (t), 49.7 (d), 116.5 (d), 124.7 (s), 128.0 (s), 128.7 (d), 129.0 (d), 138.0 (s), 167.4 (s), 204.4 (s); Anal. Calcd for $C_{13}H_{14}ClNO_2$: C, 62.03; H, 5.61; N, 5.56. Found: C, 62.09; H, 5.64; N, 5.55.

4.1.10. 6-Bromo-4-(4-chlorobenzoyl)-1-ethyl-3,4-dihydro-2(1H)-quinolinone ***6j***. White crystals; mp 145–146 °C; IR ($CHCl_3$) 3010, 1680, 1665, 1375, 1135 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.25 (t, J=7.0 Hz, 3H, CH_3), 2.86 (dd, J=16.0, 5.8 Hz, 1H, CH), 2.98 (dd, J=16.0, 5.8 Hz, 1H, CH), 3.86–4.10 (m, 2H, NCH_2), 4.78 (t, J=5.8 Hz, 1H, CH), 6.94 (d, J=8.7 Hz, 1H, ArH), 7.18 (d, J=1.8 Hz, 1H, ArH), 7.38 (dd, J=8.7, 1.8 Hz, 1H, ArH), 7.49 (d, J=8.5 Hz, 2H, ArH), 7.93 (d, J=8.5 Hz, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 12.4 (q), 34.2 (t), 37.4 (t), 42.9 (d), 115.3 (s), 117.0 (d), 125.6 (s), 129.4 (2× d), 130.0 (2× d), 131.1 (d), 131.5 (d), 133.6 (s), 139.1 (s), 140.5 (s), 167.3 (s), 196.3 (s); Anal. Calcd for $C_{18}H_{15}BrClNO_2$: C, 55.06; H, 3.85; N, 3.57. Found: C, 55.11; H, 3.86; N, 3.60.

4.1.11. 4-Acetyl-6-bromo-1-ethyl-3,4-dihydro-2(1H)-quinolinone ***6k***. White needles; mp 133–134 °C; IR ($CHCl_3$) 3015, 1715, 1675, 1370, 1135 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.19 (t, J=7.1 Hz, 3H, CH_3), 2.19 (s, 3H, CH_3), 2.69 (dd, J=16.1, 6.1 Hz, 1H, CH), 3.00 (dd, J=16.1, 2.7 Hz, 1H, CH), 3.77 (dd, J=6.1, 2.7 Hz, 1H, CH), 3.87–3.98 (m, 2H, NCH_2), 6.90–6.94 (m, 1H, ArH), 7.41–7.44 (m, 1H, ArH), 7.44 (s, 1H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 12.3 (q), 27.7 (q), 32.9 (t), 37.1 (t), 49.6 (d), 115.4 (s), 116.9 (d), 125.1 (s), 131.7 (d), 131.8 (d), 138.5 (s), 167.4 (s), 204.4 (s); Anal. Calcd for $C_{13}H_{14}BrNO_2$: C, 52.72; H, 4.76; N, 4.73. Found: C, 52.89; H, 4.80; N, 4.69.

4.1.12. 4,6-Bis(ethoxycarbonyl)-1-ethyl-3,4-dihydro-2(1H)-quinolinone ***6l***. White powder; mp 90–91 °C; IR ($CHCl_3$) 2990, 1730, 1715, 1680, 1615, 1375 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.20–1.28 (m, 6H, CH_3), 1.40 (t, J=7.1 Hz, 3H, CH_3), 2.80 (dd, J=16.1, 6.3 Hz, 1H, CH), 3.04 (dd, J=16.1, 3.9 Hz, 1H, CH), 3.89 (dd, J=6.3, 3.9 Hz, 1H, CH), 3.97–4.09 (m, 2H, NCH_2), 4.11–4.21 (m, 2H, OCH_2), 4.33–4.43 (m, 2H, OCH_2), 7.08 (d, J=8.6 Hz, 1H, ArH), 7.96 (d, J=1.9 Hz, 1H, ArH), 8.00 (dd, J=8.6, 1.9 Hz, 1H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 12.4 (q), 14.0 (q), 14.3 (q), 33.6 (t), 37.3 (t), 42.1 (d), 60.9 (t), 61.5 (t), 114.7 (d), 122.7 (s), 124.7 (s), 130.2 (d), 130.5 (d), 142.9 (s), 165.7 (s), 167.5 (s), 171.1 (s); Anal. Calcd for $C_{17}H_{21}NO_5$: C, 63.94; H, 6.63; N, 4.39. Found: C, 63.89; H, 6.65; N, 4.39.

4.1.13. 4-(4-Chlorobenzoyl)-6-ethoxycarbonyl-1-ethyl-3,4-dihydro-2(1H)-quinolinone ***6m***. White needles; mp 184–185 °C; IR ($CHCl_3$) 3010, 1710, 1685, 1375, 1265 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.27 (t, J=7.0 Hz, 3H, CH_3), 1.34 (t, J=7.1 Hz, 3H, CH_3), 2.91 (dd, J=16.1, 5.2 Hz, 1H, CH), 3.03 (dd, J=16.1, 5.2 Hz, 1H, CH), 4.05 (q, J=7.0 Hz, 2H, NCH_2), 4.31 (q, J=7.1 Hz, 2H, OCH_2), 4.86 (t, J=5.2 Hz, 1H, CH), 7.09 (d, J=8.6 Hz, 1H, ArH), 7.49 (d, J=8.6 Hz, 2H, ArH), 7.78 (s, 1H, ArH), 7.96 (d, J=8.6 Hz, 3H, ArH); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 12.4 (q), 14.2 (q), 34.1 (t), 37.4 (t), 43.1 (d), 60.9 (t), 115.0 (d), 123.0 (s), 124.6 (s), 129.3 (2× d), 139.98 (d), 130.09 (2× d), 130.4 (d), 133.5 (s), 140.4 (s), 143.7 (s), 165.6 (s), 167.7 (s), 196.4 (s); Anal. Calcd for $C_{21}H_{20}ClNO_4$: C, 65.37; H, 5.22; N, 3.63. Found: C, 65.22; H, 5.22; N, 3.59.

4.1.14. 4-(4-Chlorobenzoyl)-1-ethyl-6-methoxyl-3,4-dihydro-2(1H)-quinolinone ***6n***. White crystals; mp 119–120 °C; IR ($CHCl_3$) 3010, 1685, 1660, 1240, 1145 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.25 (t,

J=7.0 Hz, 3H, CH_3), 2.83 (dd, J=15.9, 6.0 Hz, 1H, CH), 2.98 (dd, J=15.9, 6.0 Hz, 1H, CH), 3.70 (s, 3H, OCH_3), 3.91–4.08 (m, 2H, NCH_2), 4.76 (t, J=6.0 Hz, 1H, CH), 6.60 (d, J=2.0 Hz, 1H, ArH), 6.80 (dd, J=8.8, 2.0 Hz, 1H, ArH), 6.99 (d, J=8.8 Hz, 1H, ArH), 7.47 (d, J=8.3 Hz, 2H, ArH), 7.94 (d, J=8.3 Hz, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 12.5 (q), 34.3 (t), 37.3 (t), 43.3 (d), 55.4 (q), 112.7 (d), 114.8 (d), 116.2 (d), 125.0 (s), 129.2 (2× d), 130.0 (2× d), 133.3 (s), 134.1 (s), 140.2 (s), 155.0 (s), 167.4 (s), 196.8 (s); Anal. Calcd for $C_{19}H_{18}ClNO_3$: C, 66.38; H, 5.28; N, 4.07. Found: C, 66.13; H, 5.31; N, 3.92.

4.1.15. 4-Acetyl-1-ethyl-6-methoxyl-3,4-dihydro-2(1H)-quinolinone ***6o***. White needles; mp 90–91 °C; IR ($CHCl_3$) 2975, 1710, 1655, 1385, 1225 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.19 (t, J=7.1 Hz, 3H, CH_3), 2.17 (s, 3H, CH_3), 2.69 (dd, J=16.0, 6.1 Hz, 1H, CH), 2.98 (dd, J=16.0, 2.7 Hz, 1H, CH), 3.73 (dd, J=6.1, 2.7 Hz, 1H, CH), 3.82 (s, 3H, OCH_3), 3.89–3.98 (m, 2H, NCH_2), 6.82–6.87 (m, 2H, ArH), 6.95–6.99 (m, 1H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 12.4 (q), 27.6 (q), 33.2 (t), 37.0 (t), 50.1 (d), 55.6 (q), 113.2 (d), 115.3 (d), 116.3 (d), 124.4 (s), 132.8 (s), 155.2 (s), 167.5 (s), 205.1 (s); Anal. Calcd for $C_{14}H_{17}NO_3$: C, 68.00; H, 6.93; N, 5.66. Found: C, 67.97; H, 6.93; N, 5.63.

4.1.16. 4-Ethoxycarbonyl-1-ethyl-6-methoxy-3,4-dihydro-2(1H)-quinolinone ***6p***. White needles; mp 65–66 °C; IR ($CHCl_3$) 2990, 1730, 1670, 1505, 1385 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.18–1.26 (m, 6H, CH_3), 2.76 (dd, J=16.0, 6.2 Hz, 1H, CH), 2.97 (dd, J=16.0, 4.3 Hz, 1H, CH), 3.74–3.84 (m, 1H, CH), 3.80 (s, 3H, CH_3), 3.85–4.07 (m, 2H, NCH_2), 4.15 (q, J=6.9 Hz, 2H, OCH_2), 6.83 (s, 1H, ArH), 6.84 (d, J=8.8 Hz, 1H, ArH), 6.97 (d, J=8.8 Hz, 1H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 12.5 (q), 14.0 (q), 33.9 (t), 37.2 (t), 42.6 (d), 55.6 (q), 61.4 (t), 113.6 (d), 114.6 (d), 116.1 (d), 124.4 (s), 132.6 (s), 155.2 (s), 167.1 (s), 171.4 (s); Anal. Calcd for $C_{15}H_{19}NO_4$: C, 64.97; H, 6.91; N, 5.05. Found: C, 64.95; H, 6.90; N, 5.04.

4.1.17. 4-Benzenesulfonyl-6-methoxyl-1-ethyl-3,4-dihydro-2(1H)-quinolinone ***6q***. White crystals; mp 180–181 °C; IR (KBr) 2935, 1660, 1515, 1305, 1040 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.02 (t, J=7.1 Hz, 3H, CH_3), 3.00 (dd, J=17.7, 7.8 Hz, 1H, CH), 3.16 (dq, J=14.3, 7.1 Hz, 1H, NCH), 3.33 (d, J=17.7 Hz, 1H, CH), 3.56 (dq, J=14.3, 7.1 Hz, 1H, NCH), 3.80 (s, 3H, OCH_3), 4.26 (d, J=7.8 Hz, 1H, SO_2CH), 6.74–6.80 (m, 1H, ArH), 6.90–6.95 (m, 2H, ArH), 7.43 (t, J=7.7 Hz, 2H, ArH), 7.57 (d, J=7.7 Hz, 2H, ArH), 7.59 (t, J=7.7 Hz, 1H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 12.4 (q), 31.8 (t), 37.5 (t), 55.7 (q), 63.3 (d), 116.0 (d), 116.5 (d), 116.6 (d), 117.1 (s), 128.8 (2× d), 129.5 (2× d), 133.6 (s), 134.1 (d), 136.0 (s), 155.0 (s), 164.1 (s); Anal. Calcd for $C_{18}H_{19}NO_4S$: C, 62.59; H, 5.54; N, 4.06. Found: C, 62.49; H, 5.54; N, 4.06.

4.1.18. 1-Ethyl-4-ethoxycarbonyl-1-azaspiro[4,5]deca-6,9-diene-2,8-dione ***7p***. White crystals; mp 91–92 °C; IR (KBr) 2930, 1730, 1695, 1670, 1225 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.11 (t, J=7.2 Hz, 3H, CH_3), 1.14 (t, J=7.1 Hz, 3H, CH_3), 2.67 (dd, J=17.2, 9.1 Hz, 1H, CH), 2.98–3.12 (m, 2H, 2× CH), 3.17–3.33 (m, 2H, NCH_2), 4.00–4.15 (m, 2H, OCH_2), 6.34 (dd, J=10.1, 1.9 Hz, 1H, CH), 6.45 (dd, J=10.0, 1.9 Hz, 1H, CH), 6.69 (dd, J=10.1, 3.0 Hz, 1H, CH), 6.76 (dd, J=10.0, 3.0 Hz, 1H, CH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.0 (q), 15.0 (q), 31.7 (t), 36.4 (t), 47.2 (d), 61.9 (t), 63.5 (s), 131.35 (d), 131.39 (d), 145.4 (d), 148.7 (d), 168.7 (s), 172.4 (s), 184.1 (s); Anal. Calcd for $C_{14}H_{17}NO_4$: C, 63.87; H, 6.51; N, 5.32. Found: C, 63.60; H, 6.54; N, 5.25.

4.1.19. 4-Benzenesulfonyl-1-ethyl-1-aza-spiro[4,5]-deca-6,9-diene-2,8-dione ***7q***. White crystals; mp 187–188 °C; IR (KBr) 2985, 1695, 1395, 1310, 1150 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.05 (t, J=7.1 Hz, 3H, CH_3), 2.78 (dd, J=16.8, 8.8 Hz, 1H, CH), 2.85 (dq, J=14.2, 7.1 Hz, 1H, NCH), 3.13–3.25 (m, 2H, NCH+CH), 3.95 (dd, J=11.6, 8.8 Hz, 1H, SO_2CH), 6.09 (dd, J=10.1, 1.8 Hz, 1H, CH), 6.39 (dd, J=10.1, 3.1 Hz, 1H, CH), 6.46 (dd, J=10.1, 1.8 Hz, 1H, CH), 7.01 (dd, J=10.1, 3.1 Hz, 1H, CH), 7.54 (t, J=7.6 Hz, 2H, ArH), 7.69 (t, J=7.6 Hz, 1H, ArH), 7.80 (d, J=7.6 Hz, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.9 (q), 30.5 (t), 35.9 (t), 62.3 (s), 64.9 (d), 128.6 (2× d), 129.7 (2× d), 131.3 (d), 131.8 (d), 134.8 (d), 137.7 (s), 143.2 (d), 145.8 (d), 169.7 (s), 183.7 (s); Anal. Calcd for $C_{17}H_{17}NO_4S$: C, 61.61; H, 5.17; N, 4.23. Found: C, 61.63; H, 5.20; N, 4.24.

4.1.20. 1-Ethyl-1-azaspiro[4.5]deca-6,9-diene-2,8-dione ***7r***. White crystals; mp 98–99 °C; IR (KBr) 2980, 1695, 1400, 1130, 865 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.10 (t, J=7.2 Hz, 3H, CH_3), 2.17 (t, J=8.1 Hz, 2H, CH_2), 2.58 (t, J=8.1 Hz, 2H, CH_2), 3.15 (q, J=7.2 Hz, 2H, NCH_2), 6.34 (d, J=10.1 Hz, 2H, 2× CH), 6.78 (d, J=10.1 Hz, 2H, 2× CH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.9 (q), 29.2 (t), 30.0 (t), 36.0 (t), 62.2 (s), 129.8 (2× d), 149.5 (2× d), 174.2 (s), 184.2 (s); Anal. Calcd for $C_{11}H_{13}NO_2$: C, 69.09; H, 6.85; N, 7.32. Found: C, 68.91; H, 6.86; N, 7.25.

4.1.21. 1-Ethyl-4-methyl-1-azaspiro[4.5]deca-6,9-diene-2,8-dione ***7s***. White crystals; mp 102–103 °C; IR (KBr) 2970, 1670, 1400, 1140, 890 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.96 (d, J=7.0 Hz, 3H, CH_3), 1.10 (t, J=7.1 Hz, 3H, CH_3), 2.24 (dd, J=16.4, 11.5 Hz, 1H, CH), 2.42–2.53 (m, 1H, CH), 2.67 (dd, J=16.4, 8.2 Hz, 1H, CH), 3.07 (dq, J=14.2, 7.1 Hz, 1H, NCH), 3.23 (dq, J=14.2, 7.1 Hz, 1H, NCH), 6.39–6.44 (m, 2H, 2× CH), 6.66–6.72 (m, 2H, 2× CH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 13.6 (q), 14.7 (q), 36.2 (t), 37.2 (t), 37.6 (d), 65.9 (s), 131.0 (d), 131.2 (d), 146.8 (d), 149.0 (d), 173.7 (s), 184.4 (s); Anal. Calcd for $C_{12}H_{15}NO_2$: C, 70.22; H, 7.37; N, 6.82. Found: C, 70.01; H, 7.42; N, 6.71.

4.1.22. 1-(2,4,6-Trimethylbenzyl)-1-aza-spiro[4,5]-deca-6,9-diene-2,8-dione ***7t***. White crystals; mp 157–158 °C; IR (KBr) 2985, 1695, 1395, 1310, 1150 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.04 (t, J=8.1 Hz, 2H, CH_2), 2.15 (s, 6H, 2× CH_3), 2.23 (s, 3H, CH_3), 2.64 (t, J=8.1 Hz, 2H, CH_2), 4.51 (s, 2H, NCH_2), 6.01 (d, J=10.1 Hz, 2H, CH_2), 6.44 (d, J=10.1 Hz, 2H, CH_2), 6.73 (s, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 20.1 (2× q), 20.8 (q), 29.4 (t), 30.8 (t), 39.4 (t), 62.2 (s), 128.9 (2× d), 129.2 (2× d), 129.9 (s), 137.62 (s), 137.67 (2× s), 149.5 (2× d), 174.0 (s), 184.4 (s); Anal. Calcd for $C_{19}H_{21}NO_2$: C, 77.26; H, 7.17; N, 4.74. Found: C, 76.90; H, 7.17; N, 4.74.

4.1.23. 4-Methyl-1-(2,4,6-trimethylbenzyl)-1-aza-spiro[4,5]-deca-6,9-diene-2,8-dione ***7u***. White crystals; mp 127–128 °C; IR (KBr) 2960, 1700, 1670, 1380 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.15 (s, 6H, 2× CH_3), 2.23 (s, 3H, CH_3), 2.23–2.39 (m, 4H, CH+CH_3), 2.68–2.83 (m, 2H, CH_2), 4.10 (d, J=15.1 Hz, 1H, NCH), 4.91 (d, J=15.1 Hz, 1H, NCH), 5.88 (dd, J=10.2, 2.0 Hz, 1H, CH), 6.02 (dd, J=10.2, 3.0 Hz, 1H, CH), 6.32 (dd, J=10.2, 2.0 Hz, 1H, CH), 6.61 (dd, J=10.2, 3.0 Hz, 1H, CH), 6.73 (s, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 13.6 (q), 20.0 (2× q), 20.8 (q), 37.6 (t), 37.7 (t), 39.5 (t), 66.2 (s), 128.9 (d), 129.2 (2× d), 130.1 (s), 132.0 (d), 137.6 (s), 137.7 (2× s), 146.7 (d), 149.2 (d), 173.7 (s), 184.7 (s); Anal. Calcd for $C_{20}H_{23}NO_2$: C, 77.64; H, 7.49; N, 4.53. Found: C, 77.70; H, 7.52; N, 4.48.

4.1.24. 4-Benzenesulfonyl-1-(2,4,6-trimethylbenzyl)-1-aza-spiro[4,5]-deca-6,9-diene-2,8-dione ***7v***. White crystals; mp 210–211 °C; IR (KBr) 2985, 1695, 1395, 1310, 1150 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.08 (s, 6H, 2× CH_3), 2.20 (s, 3H, CH_3), 2.88 (dd, J=17.1, 8.8 Hz, 1H, CH), 3.26 (dd, J=17.1, 11.2 Hz, 1H, CH), 3.79 (dd, J=11.2, 8.8 Hz, 1H, SO_2CH), 4.11 (d, J=15.3 Hz, 1H, NCH), 4.83 (d, J=15.3 Hz, 1H, NCH), 5.52 (dd, J=10.1, 1.9 Hz, 1H, CH), 5.78 (dd, J=10.1, 3.1 Hz, 1H, CH), 6.36 (dd, J=10.2, 1.9 Hz, 1H, CH), 6.69 (s, 2H, ArH), 6.90 (dd, J=10.2, 3.1 Hz, 1H, CH), 7.49 (t, J=7.7 Hz, 2H, ArH), 7.63 (t, J=7.7 Hz, 1H, ArH), 7.72 (d, J=7.7 Hz, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 20.1 (2× q), 20.8 (q), 30.6 (t), 39.2 (t), 62.3 (s), 64.2 (d), 128.5 (2× d), 129.33 (2× d), 129.37 (s), 129.6 (3× d), 132.0 (d), 134.7 (d), 137.5 (2× s), 137.7 (s), 137.8 (s), 142.9 (d), 145.5 (d), 169.4 (s), 183.8 (s); Anal. Calcd for

$C_{25}H_{25}NO_4S$: C, 68.94; H, 5.79; N, 3.22. Found: C, 68.97; H, 5.72; N, 3.23.

4.1.25. rel-(1R,3′S)-3′-(Benzenesulfonyl)-1′-ethyl-4H-spiro[naphthalene-1,2′-pyrrolidin]-4,5′-dione ***9a***. White needles; mp 164–165 °C; IR (KBr) 1700, 1300, 1155, 1085, 590 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, J=7.1 Hz, 3H, CH_3), 2.77 (dq, J=14.2, 7.1 Hz, 1H, NCH), 2.95 (dq, J=14.2, 7.1 Hz, 1H, NCH), 3.02 (dd, J=17.0, 8.7 Hz, 1H, CH), 3.37 (dd, J=17.0, 11.0 Hz, 1H, CH), 4.36 (dd, J=11.4, 8.7 Hz, 1H, CH), 6.60 (d, J=10.3 Hz, 1H, CH), 7.07 (d, J=10.3 Hz, 1H, CH), 7.24 (t, J=7.7 Hz, 2H, ArH), 7.36 (d, J=7.7 Hz, 1H, ArH), 7.40 (t, J=7.7 Hz, 1H, ArH), 7.465 (t, J=7.7 Hz, 1H, ArH), 7.473 (d, J=7.7 Hz, 2H, ArH), 7.60 (t, J=7.7 Hz, 1H, ArH), 7.85 (d, J=7.7 Hz, 1H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 13.8 (q), 30.1 (t), 36.6 (t), 63.7 (s), 68.2 (d), 126.0 (d), 127.0 (d), 128.0 (2× d), 129.1 (d), 129.2 (2× d), 131.2 (d), 131.6 (s), 133.3 (d), 134.1 (d), 137.1 (s), 140.7 (s), 143.7 (d), 170.2 (s), 182.2 (s); Anal. Calcd for $C_{21}H_{19}NO_4S$: C, 66.12; H, 5.02; N, 3.67. Found: C, 65.76; H, 4.92; N, 3.58.

4.1.26. rel-(1R,3′S)-3′-Ethoxycarbonyl-1′-ethyl-4H-spiro[naphthalene-1,2′-pyrrolidin]-4,5′-dione ***9b***. White crystals; mp 136–137 °C; IR (KBr) 1730, 1695, 1600, 1235, 770 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.98 (t, J=7.1 Hz, 6H, 2× CH_3), 2.78 (dd, J=17.4, 9.4 Hz, 1H, CH), 2.84 (dq, J=14.3, 7.1 Hz, 1H, NCH), 3.17 (dd, J=17.4, 11.0 Hz, 1H, CH), 3.24 (dq, J=14.3, 7.1 Hz, 1H, NCH), 3.54 (dd, J=11.0, 9.4 Hz, 1H, CH), 3.87–4.04 (m, 2H, OCH_2), 6.52 (d, J=10.3 Hz, 1H, CH), 6.83 (d, J=10.3 Hz, 1H, CH), 7.51 (d, J=7.7 Hz, 1H, ArH), 7.55 (t, J=7.7 Hz, 1H, ArH), 7.71 (t, J=7.7 Hz, 1H, ArH), 8.20 (d, J=7.7 Hz, 1H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 13.7 (q), 13.9 (q), 31.9 (t), 36.7 (t), 52.4 (d), 61.6 (t), 65.0 (s), 126.3 (d), 126.8 (d), 128.9 (d), 131.0 (d), 132.0 (s), 133.6 (d), 142.9 (s), 146.2 (d), 168.9 (s), 173.0 (s), 183.0 (s); Anal. Calcd for $C_{18}H_{19}NO_4$: C, 68.99: H, 6.11; N, 4.47. Found: C, 68.80; H, 6.14; N, 4.43.

4.1.27. 1′-Ethyl-4H-spiro[naphthalene-1,2′-pyrrolidin]-4,5′-dione ***9c***. White powder; mp 123–124 °C; IR (KBr) 2980, 1675, 1455, 1300, 775 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.97 (t, J=7.1 Hz, 3H, CH_3), 2.25–2.40 (m, 2H, CH_2), 2.63–2.81 (m, 2H, CH_2), 2.84 (dq, J=14.3, 7.1 Hz, 1H, NCH), 3.27 (dq, J=14.3, 7.1 Hz, 1H, NCH), 6.50 (d, J=10.2 Hz, 1H, CH), 6.94 (d, J=10.2 Hz, 1H, CH), 7.39 (d, J=7.8 Hz, 1H, ArH), 7.50 (dt, J=7.8, 1.2 Hz, 1H, ArH), 7.64 (dt, J=7.8, 1.2 Hz, 1H, ArH), 8.19 (dd, J=7.8, 1.2 Hz, 1H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.2 (q), 29.5 (t), 34.3 (t), 36.4 (t), 63.6 (s), 126.0 (d), 127.0 (d), 128.5 (d), 128.8 (d), 131.0 (s), 133.5 (d), 144.5 (s), 150.8 (d), 174.9 (s), 183.3 (s); Anal. Calcd for $C_{15}H_{15}NO_2$: C, 74.67; H, 6.27; N, 5.81. Found: C, 74.35; H, 6.33; N, 5.65.

4.1.28. rel-(1S,3′S)-3′-(Benzenesulfonyl)-1′-ethyl-4H-spiro[naphthalene-1,2′-pyrrolidine]-4,5′-dione ***10a***. White needles; mp 167–168 °C; IR (KBr) 1685, 1295, 1150, 1085, 585 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.00 (t, J=7.2 Hz, 3H, CH_3), 2.69 (dq, J=14.3, 7.2 Hz, 1H, NCH), 2.84 (dd, J=16.9, 9.3 Hz, 1H, CH), 3.29 (dq, J=14.3, 7.2 Hz, 1H, NCH), 3.36 (dd, J=16.9, 11.5 Hz, 1H, CH), 4.04 (dd, J=11.5, 9.3 Hz, 1H, CH), 6.47 (d, J=10.1 Hz, 1H, CH), 6.72 (d, J=10.1 Hz, 1H, ArH), 7.24–7.30 (m, 1H, ArH), 7.40–7.47 (m, 4H, ArH), 7.55–7.64 (m, 3H, ArH), 8.16–8.22 (m, 1H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.5 (q), 31.5 (t), 36.7 (t), 64.3 (d), 64.5 (s), 127.1 (d), 128.0 (d), 128.2 (2× d), 129.4 (2× d), 129.9 (d), 131.4 (d), 132.4 (d), 132.7 (s), 134.3 (d), 136.7 (s), 138.0 (s), 147.8 (d), 170.3 (s), 182.6 (s); Anal. Calcd for $C_{21}H_{19}NO_4S$: C, 66.12; H, 5.02; N, 3.67. Found C, 65.88; H, 4.97; N, 3.62.

4.1.29. rel-(1S,3′S)-3′-Ethoxycarbonyl-1′-ethyl-4H-spiro[naphthalene-1,2′-pyrrolidin]-4,5′-dione ***10b***. White needles; mp 140–141 °C; IR (KBr) 1735, 1695, 1600, 1215, 770 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.80 (t, J=7.2 Hz, 3H, CH_3), 1.03 (t, J=7.2 Hz, 3H, CH_3), 2.74 (dd, J=17.2, 9.8 Hz, 1H, CH), 2.84 (dq, J=14.3, 7.2 Hz, 1H, NCH), 3.27–3.40 (m, 2H, NCH+CH), 3.40–3.51 (m, 2H, OCH+CH), 3.63–3.72 (m, 1H, OCH), 6.62 (d, J=10.1 Hz, 1H, CH), 6.93 (d, J=10.1 Hz, 1H, CH), 7.21 (d, J=7.7 Hz, 1H, ArH), 7.50 (t, J=7.7 Hz, 1H, ArH), 7.58 (t, J=7.7 Hz, 1H, ArH), 8.16 (d, J=7.7 Hz, 1H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 13.3 (q), 14.5 (q), 31.5 (t), 37.0 (t), 47.9 (d), 61.5 (t), 65.5 (s), 126.1 (d), 126.9 (d), 129.2 (d), 130.3 (d), 132.0 (s), 132.9 (d), 139.9 (s), 150.2 (d), 168.4 (s), 173.1 (s), 183.4 (s); Anal. Calcd for $C_{18}H_{19}NO_4$: C, 68.99: H, 6.11; N, 4.47. Found: C, 68.73; H, 6.10; N, 4.46.

4.1.30. 1′-Benzyl-1′H,4H-spiro[cyclohexa-2,5-diene-1,4′quinoline]-2′,4(3′H)-dione ***17a***. White crystals; mp 139–140 °C; IR (KBr) 1665, 1630, 1380, 1295, 850 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.92 (s, 2H, CH_2), 5.26 (s, 2H, NCH_2), 6.39 (d, J=10.3 Hz, 2H, CH), 6.97 (d, J=10.3 Hz, 2H, CH), 7.03 (t, J=7.8 Hz, 1H, ArH), 7.04 (t, J=7.8 Hz, 1H, ArH), 7.08 (dd, J=7.8, 1.5 Hz, 1H, ArH), 7.23 (td, J=7.8, 1.5 Hz, 1H, ArH), 7.25–7.30 (m, 3H, ArH), 7.31–7.37 (m, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 40.7 (t), 43.1 (s), 46.3 (t), 116.5 (d), 124.0 (s), 124.4 (s), 126.5 (2× d), 126.6 (d), 127.4 (d), 128.8 (2× d), 129.3 (d), 129.5 (2× d), 136.2 (s), 139.0 (s), 149.1 (2× d), 166.7 (s), 184.8 (s); Anal. Calcd for $C_{21}H_{17}NO_2$: C, 79.98; H, 5.43; N, 4.44. Found: C, 79.65; H, 5.31; N, 4.36.

4.1.31. 1′-Benzyl-6′-methyl-1′H,4H-spiro[cyclohexa-2,5-diene-1,4′quinoline]-2′,4(3′H)-dione ***17b***. White crystals; mp 185–186 °C; IR (KBr) 1665, 1500, 1375, 1220, 860 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.23 (s, 3H, CH_3), 2.90 (s, 2H, CH_2), 5.24 (s, 2H, NCH_2), 6.40 (d, J=10.1 Hz, 2H, CH), 6.86 (d, J=1.6 Hz, 1H, ArH), 6.93 (d, J=8.3 Hz, 1H, ArH), 6.96 (d, J=10.1 Hz, 2H, CH), 7.02 (dd, J=8.3, 1.6 Hz, 1H, ArH), 7.24–7.29 (m, 3H, ArH), 7.31–7.37 (m, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 20.5 (q), 40.9 (t), 43.2 (s), 46.3 (t), 116.5 (d), 124.2 (s), 126.6 (2× d), 127.2 (d), 127.4 (d), 128.8 (2× d), 129.5 (2× d), 129.8 (d), 133.8 (s), 136.4 (s), 136.6 (s), 149.4 (2× d), 166.7 (s), 184.9 (s); Anal. Calcd for $C_{22}H_{19}NO_2$: C, 80.22; H, 5.81; N, 4.25. Found: C, 80.27; H, 5.79; N, 4.16.

4.1.32. 1′-Benzyl-6′-chloro-1′H,4H-spiro[cyclohexa-2,5-diene-1,4′quinoline]-2′,4(3′H)-dione ***17c***. White crystals; mp 208–209 °C; IR (KBr) 1680, 1490, 1370, 1225, 860 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.92 (s, 2H, CH_2), 5.24 (s, 2H, NCH_2), 6.43 (d, J=10.1 Hz, 2H, CH), 6.93 (d, J=10.1 Hz, 2H, CH), 6.96 (d, J=8.8 Hz, 1H, ArH), 7.04 (d, J=2.6 Hz, 1H, ArH), 7.19 (dd, J=8.8, 2.6 Hz, 1H, ArH), 7.22–7.31 (m, 3H, ArH), 7.32–7.38 (m, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 40.5 (t), 42.9 (s), 46.3 (t), 117.8 (d), 126.2 (s), 126.5 (2× d), 126.6 (d), 127.6 (d), 129.0 (2× d), 129.2 (s), 129.3 (d), 130.0 (2× d), 135.8 (s), 137.6 (s), 148.2 (2× d), 166.4 (s), 184.4 (s); Anal. Calcd for $C_{21}H_{16}ClNO_2$: C, 72.10; H, 4.61; N, 4.00. Found: C, 72.00; H, 4.67; N, 4.00.

4.1.33. 1′-Benzyl-3-methyl-1′H,4H-spiro[cyclohexa-2,5-diene-1,4′quinoline]-2′,4(3′H)-dione ***17d***. White crystals; mp 162–163 °C; IR (KBr) 1665, 1635, 1495, 1380, 765 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.94 (d, J=1.4 Hz, 3H, CH_3), 2.86 (d, J=15.4 Hz, 1H, CH), 2.93 (d, J=15.4 Hz, 1H, CH), 5.22 (d, J=16 Hz, 1H, NCH), 5.32 (d, J=16 Hz, 1H, NCH), 6.41 (d, J=9.9 Hz, 1H, CH), 6.71–6.75 (m, 1H, CH), 6.94 (dd, J=9.9, 3.0 Hz, 1H, CH), 7.01 (t, J=7.8 Hz, 1H, ArH), 7.03 (d, J=7.8 Hz, 1H, ArH), 7.07 (dd, J=7.8, 1.6 Hz, 1H, ArH), 7.22 (td, J=7.8, 1.6 Hz, 1H, ArH), 7.27–7.31 (m, 3H, ArH), 7.32–7.38 (m, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 16.0 (q), 41.0 (t), 43.2 (s), 46.3 (t), 116.5 (d), 123.9 (d), 125.1 (s), 126.4 (d), 126.5 (2× d), 127.4 (d), 128.8 (2× d), 129.1 (d), 129.4 (d), 135.8 (s), 136.4 (s), 139.0 (s), 144.4 (d), 149.0 (d), 167.1 (s), 185.5 (s); Anal. Calcd for $C_{22}H_{19}NO_2$: C, 80.22; H, 5.81; N, 4.25. Found: C, 80.28; H, 5.78; N, 4.18.

4.1.34. 1′-Benzyl-3,6′-dimethyl-1′H,4H-spiro[cyclohexa-2,5-diene-1,4′quinoline]-2′,4(3′H)-dione ***17e***. White powder; mp 125–126 °C; IR (KBr) 1665, 1640, 1500, 1380, 725 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.94 (d, J=1.2 Hz, 3H, CH_3), 2.23 (s, 3H, CH_3), 2.83 (d,

J=15.5 Hz, 1H, CH), 2.90 (d, *J*=15.5 Hz, 1H, CH), 5.19 (d, *J*=15.9 Hz, 1H, NCH), 5.29 (d, *J*=15.9 Hz, 1H, NCH), 6.41 (d, *J*=9.6 Hz, 1H, CH), 6.69–6.73 (m, 1H, CH), 6.84 (d, *J*=1.3 Hz, 1H, ArH), 6.92 (d, *J*=8.3 Hz, 1H, ArH), 6.93 (dd, *J*=9.6, 3.7 Hz, 1H, CH), 7.01 (dd, *J*=8.3, 1.3 Hz, 1H, ArH), 7.25–7.29 (m, 3H, ArH), 7.31–7.37 (m, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 16.0 (q), 20.5 (q), 41.1 (t), 43.2 (s), 46.3 (t), 116.5 (d), 125.0 (s), 126.6 (2× d), 127.0 (d), 127.4 (d), 128.8 (2× d), 129.4 (d), 129.6 (d), 133.7 (s), 135.8 (s), 136.5 (s), 136.7 (s), 144.6 (d), 149.3 (d), 167.1 (s), 185.7 (s); HRMS (EI) calcd for $C_{23}H_{21}NO_2Na$ *m*/*e* 366.1470, found: 366.1472.

4.1.35. 1′-Benzyl-6′-chloro-3-methyl-1′H,4H-spiro[cyclohexa-2,5-diene-1,4′quinoline]-2′,4(3′H)-dione ***17f***. White crystals; mp 185–186 °C; IR (KBr) 1665, 1640, 1420, 1375, 720 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.95 (d, *J*=1.4 Hz, 3H, CH_3), 2.86 (d, *J*=15.6 Hz, 1H, CH), 2.92 (d, *J*=15.6 Hz, 1H, CH), 5.20 (d, *J*=16 Hz, 1H, NCH), 5.29 (d, *J*=16 Hz, 1H, NCH), 6.43 (d, *J*=9.9 Hz, 1H, CH), 6.67–6.70 (m, 1H, CH), 6.90 (dd, *J*=9.9, 3.1 Hz, 1H, CH), 6.96 (d, *J*=8.8 Hz, 1H, ArH), 7.03 (d, *J*=2.4 Hz, 1H, ArH), 7.17 (dd, *J*=8.8, 2.4 Hz, 1H, ArH), 7.23–7.31 (m, 3H, ArH), 7.32–7.38 (m, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 16.0 (q), 40.8 (t), 43.0 (s), 46.3 (t), 117.8 (d), 126.49 (d), 126.57 (2× d), 127.0 (s), 127.6 (d), 128.92 (2× d), 128.96 (d), 129.2 (s), 129.9 (d), 136.0 (s), 136.5 (s), 137.7 (s), 143.3 (d), 148.0 (d), 166.8 (s), 185.2 (s); Anal. Calcd for $C_{22}H_{18}ClNO_2$: C, 72.62; H, 4.99; N, 3.85. Found: C, 72.33; H, 5.09; N, 3.83.

4.1.36. 1′-Benzyl-3′-methyl-1′H,4H-spiro[cyclohexa-2,5-diene-1,4′quinoline]-2′,4(3′H)-dione ***17g***. White crystals; mp 139–140 °C; IR (KBr) 1665, 1490, 1450, 1375, 850 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.24 (d, *J*=7.0 Hz, 3H, CH_3), 3.04 (q, *J*=7.0 Hz, 1H, CH), 5.02 (d, *J*=16.1 Hz, 1H, NCH), 5.49 (d, *J*=16.1 Hz, 1H, NCH), 6.32 (dd, *J*=10.1, 1.7 Hz, 1H, CH), 6.62 (dd, *J*=10.1, 1.7 Hz, 1H, CH), 6.80 (dd, *J*=10.1, 3.1 Hz, 1H, CH), 6.94 (dd, *J*=10.1, 3.1 Hz, 1H, CH), 6.98–7.06 (m, 2H, ArH), 7.09 (dd, *J*=7.6, 1.3 Hz, 1H, ArH), 7.20–7.30 (m, 4H, ArH), 7.32–7.37 (m, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 10.6 (q), 42.4 (d), 46.9 (t), 47.6 (s), 116.5 (d), 123.9 (d), 125.0 (s), 126.5 (2× d), 126.7 (d), 127.4 (d), 128.8 (2× d), 129.4 (d), 130.2 (d), 131.6 (d), 136.5 (s), 139.0 (s), 146.6 (d), 150.6 (d), 169.8 (s), 185.3 (s); Anal. Calcd for $C_{22}H_{19}NO_2$: C, 80.22; H, 5.87; N, 4.25. Found: C, 80.29; H, 5.74; N, 4.14.

4.1.37. 1′-Benzyl-3′,6′-dimethyl-1′H,4H-spiro[cyclohexa-2,5-diene-1,4′quinoline]-2′,4(3′H)-dione ***17h***. White crystals; mp 184–185 °C; IR (KBr) 1670, 1500, 1375, 1215, 815 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.23 (d, *J*=7.1 Hz, 3H, CH_3), 2.23 (s, 3H, CH_3), 3.01 (q, *J*=7.1 Hz, 1H, CH), 5.03 (d, *J*=16.1 Hz, 1H, NCH), 5.44 (d, *J*=16.1 Hz, 1H, NCH), 6.31 (dd, *J*=10.2, 1.8 Hz, 1H, CH), 6.61 (dd, *J*=10.2, 1.8 Hz, 1H, CH), 6.78 (dd, *J*=10.2, 3.1 Hz, 1H, CH), 6.87 (d, *J*=1.3 Hz, 1H, ArH), 6.92 (d, *J*=8.3 Hz, 1H, ArH), 6.93 (dd, *J*=10.2, 3.1 Hz, 1H, CH), 7.03 (dd, *J*=8.3, 1.3 Hz, 1H, ArH), 7.24–7.29 (m, 3H, ArH), 7.31–7.37 (m, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 10.6 (q), 20.5 (q) 42.5 (d), 46.9 (t), 47.6 (s), 116.4 (d), 124.9 (s), 126.6 (2× d), 127.3 (d), 127.4 (d), 128.8 (2× d), 129.8 (d), 130.2 (d), 131.6 (d), 133.7 (s), 136.6 (s), 136.7 (s), 146.8 (d), 150.8 (d), 169.7 (s), 185.4 (s); Anal. Calcd for $C_{23}H_{21}NO_2$: C, 80.44; H, 6.16; N, 4.08. Found: C, 80.44; H, 6.18; N, 3.99.

4.1.38. 1′-Benzyl-6′-chloro-3′-methyl-1′H,4H-spiro[cyclohexa-2,5-diene-1,4′quinoline]-2′,4(3′H)-dione ***17i***. White crystals; mp 163–164 °C; IR (KBr) 1665, 1630, 1370, 1255, 820 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.23 (d, *J*=7.0 Hz, 3H, CH_3), 3.02 (q, *J*=7.0 Hz, 1H, CH), 5.04 (d, *J*=16.1 Hz, 1H, NCH), 5.43 (d, *J*=16.1 Hz, 1H, NCH), 6.34 (dd, *J*=10.1, 1.7 Hz, 1H, CH), 6.63 (dd, *J*=10.1, 1.7 Hz, 1H, CH), 6.75 (dd, *J*=10.1, 3.2 Hz, 1H, CH), 6.90 (dd, *J*=10.1, 3.2 Hz, 1H, CH), 6.96 (d, *J*=8.6 Hz, 1H, ArH), 7.05 (d, *J*=2.5 Hz, 1H, ArH), 7.19 (dd, *J*=8.6, 2.5 Hz, 1H, ArH), 7.21–7.31 (m, 3H, ArH), 7.32–7.38 (m, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 10.6 (q), 42.3 (d), 46.9 (t), 47.3 (s), 117.7 (d), 126.5 (2× d), 126.7 (d), 126.8 (s), 127.6 (d), 128.9 (2× d), 129.12 (s), 129.19 (d), 130.7 (d), 132.1 (d), 136.1 (s), 137.6 (s) 145.6 (d), 149.5 (d), 169.5 (s), 184.9 (s); Anal. Calcd for $C_{22}H_{18}ClNO_2$: C, 72.62; H, 4.99; N, 3.85. Found: C, 72.48; H, 4.88; N, 3.81.

4.1.39. N-Benzyl-9-methoxy-5H-dibenzo[b,d]azepin-6(7H)-one ***18a***. White powder; mp 180–181 °C; IR (KBr) 1665, 1485, 1375, 1255, 855 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.51 (d, *J*=12.1 Hz, 1H, CH), 3.59 (d, *J*=12.1 Hz, 1H, CH), 3.88 (s, 3H, OCH_3), 4.92 (d, *J*=15.6 Hz, 1H, NCH), 5.17 (d, *J*=15.6 Hz, 1H, NCH), 6.89–6.93 (m, 2H, ArH), 6.95 (s, 1H, ArH), 6.97–6.98 (m, 1H, ArH), 7.10–7.15 (m, 3H, ArH), 7.22 (td, *J*=7.7, 1.6 Hz, 1H, ArH), 7.27 (td, *J*=7.7, 1.6 Hz, 1H, ArH), 7.32 (dd, *J*=7.7, 1.6 Hz, 1H, ArH), 7.43 (d, *J*=8.2 Hz, 1H, ArH), 7.47 (dd, *J*=7.7, 1.6 Hz, 1H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 42.4 (t), 51.8 (t), 55.4 (q), 112.3 (d), 114.1 (d), 123.1 (d), 125.6 (d), 126.78 (d), 126.80 (2× d), 127.7 (d), 128.3 (2× d), 129.06 (d), 129.09 (s), 129.7 (d), 134.6 (s), 136.5 (s), 137.4 (s), 140.2 (s), 160.3 (s), 170.8 (s); HMRS(EI) calcd for $C_{22}H_{19}NO_2$ *m*/*e* 329.1416, found *m*/*e* 329.1411.

4.1.40. N-Benzyl-9-methoxy-2-methyl-5H-dibenzo[b,d]azepin-6(7H)-one ***18b***. White powder; mp 146–147 °C; IR (KBr) 1660, 1605, 1380, 1235, 845 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.35 (s, 3H, CH_3), 3.51 (d, *J*=12.2 Hz, 1H, CH), 3.57 (d, *J*=12.2 Hz, 1H, CH), 3.87 (s, 3H, OCH_3), 4.88 (d, *J*=15.7 Hz, 1H, NCH), 5.16 (d, *J*=15.7 Hz, 1H, NCH), 6.87–6.92 (m, 2H, ArH), 6.94 (s, 1H, ArH), 6.95–6.97 (m, 1H, ArH), 7.07 (dd, *J*=8.3, 1.7 Hz, 1H, ArH), 7.10–7.15 (m, 3H, ArH), 7.20 (d, *J*=8.3 Hz, 1H, ArH), 7.25 (s, 1H, ArH), 7.42 (d, *J*=8.3 Hz, 1H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 20.9 (q), 42.5 (t), 51.7 (t), 55.4 (q), 112.3 (d), 114.1 (d), 122.9 (d), 126.7 (d), 126.8 (2× d), 128.2 (2× d), 128.5 (d), 129.0 (d), 129.2 (s), 130.2 (d), 134.3 (s), 135.2 (s), 136.5 (s), 137.5 (s), 137.8 (s), 160.2 (s), 170.8 (s); Anal. Calcd for $C_{23}H_{21}NO_2$: C, 80.44; H, 6.16 N, 4.08. Found: C, 80.07; H, 6.19; N, 3.98.

4.1.41. N-Benzyl-2-chloro-9-methoxy-5H-dibenzo[b,d]azepin-6(7H)-one ***18c***. White powder; mp 161–162 °C; IR (KBr) 1670, 1605, 1310, 1245, 810 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.48 (d, *J*=12.5 Hz, 1H, CH), 3.60 (d, *J*=12.5 Hz, 1H, CH), 3.88 (s, 3H, OCH_3), 4.85 (d, *J*=15.6 Hz, 1H, NCH), 5.18 (d, *J*=15.6 Hz, 1H, NCH), 6.86–6.90 (m, 2H, ArH), 6.93–6.99 (m, 2H, ArH), 7.11–7.16 (m, 3H, ArH), 7.22 (dd, *J*=8.5, 2.3 Hz, 1H, ArH), 7.26 (d, *J*=8.5 Hz, 1H, ArH), 7.40 (d, *J*=8.5 Hz, 1H, ArH), 7.44 (d, *J*=2.3 Hz, 1H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 42.3 (t), 51.7 (t), 55.5 (q), 112.6 (d), 114.3 (d), 124.6 (d), 126.8 (2× d), 127.0 (d), 127.6 (d), 127.9 (s), 128.4 (2× d), 129.0 (d), 129.4 (d), 130.8 (s), 136.2 (s), 136.5 (s), 137.0 (s), 138.6 (s), 160.7 (s), 170.5 (s); HMRS (EI) calcd for $C_{22}H_{18}ClNO_2$ *m*/*e* 363.1026, found *m*/*e* 363.1021.

4.1.42. N-Benzyl-9-methoxy-10-methyl-5H-dibenzo[b,d]azepin-6(7H)-one ***18d***. White powder; mp 126–127 °C; IR (KBr) 1665, 1605, 1380, 1270, 705 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.29 (s, 3H, CH_3), 3.48 (d, *J*=12.1 Hz, 1H, CH), 3.58 (d, *J*=12.1 Hz, 1H, CH), 3.91 (s, 3H, OCH_3), 4.96 (d, *J*=15.8 Hz, 1H, NCH), 5.09 (d, *J*=15.8 Hz, 1H, NCH), 6.86 (s, 1H, ArH), 6.91–6.96 (m, 2H, ArH), 7.12–7.17 (m, 3H, ArH), 7.23 (td, *J*=7.4, 1.9 Hz, 1H, ArH), 7.24–7.27 (m, 1H, ArH), 7.28–7.32 (m, 2H, ArH), 7.49 (dd, *J*=7.2, 2.0 Hz, 1H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 16.1 (q), 42.2 (t), 51.9 (t), 55.5 (q), 109.1 (d), 123.1 (d), 125.5 (d), 126.1 (s), 126.8 (2× d), 127.5 (2× d), 128.28 (2× d), 128.34 (s), 129.7 (d), 130.0 (d), 133.8 (s), 134.7 (s), 137.6 (s), 140.3 (s), 158.5 (s), 171.1 (s); HMRS (EI) calcd for $C_{23}H_{22}NO_2$ *m*/*e* 344.1649, found *m*/*e* 344.1650.

4.1.43. N-Benzyl-9-methoxy-2,10-dimethyl-5H-dibenzo[b,d]azepin-6(7H)-one ***18e***. White powder; mp 117–118 °C; IR (KBr) 1665, 1605, 1375, 1235, 875 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.29 (s, 3H, CH_3), 2.36 (s, 3H, CH_3), 3.48 (d, *J*=12.3 Hz, 1H, CH), 3.55 (d, *J*=12.3 Hz, 1H, CH), 3.90 (s, 3H, OCH_3), 4.92 (d, *J*=15.8 Hz, 1H, NCH), 5.09 (d, *J*=15.8 Hz, 1H, NCH), 6.85 (s, 1H, ArH), 6.90–6.94 (m, 2H, ArH),

7.03–7.07 (m, 1H, ArH), 7.11–7.15 (m, 2H, ArH), 7.18 (d, J=8.6 Hz, 1H, ArH), 7.25–7.29 (m, 3H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 16.1 (q), 20.9 (q), 42.3 (t), 51.8 (t), 55.5 (q), 109.1 (d), 122.9 (d), 126.0 (s), 126.7 (d), 126.8 (2× d), 128.26 (2× d), 128.33 (d), 128.5 (s), 129.9 (d), 130.1 (d), 133.8 (s), 134.4 (s), 135.1 (s), 137.7 (s), 137.9 (s), 158.4 (s), 171.1 (s); HMRS (EI) calcd for $C_{24}H_{23}NO_2$ m/e 357.1729, found m/e 357.1727.

4.1.44. N-Benzyl-2-chloro-9-methoxy-10-methyl-5H-dibenzo[b,d] azepin-6(7H)-one ***18f***. White powder; mp 129–130 °C; IR (KBr) 1672, 1483, 1376, 1260, 872 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.28 (s, 3H, CH_3), 3.45 (d, J=12.5 Hz, 1H, CH), 3.58 (d, J=12.5 Hz, 1H, CH), 3.91 (s, 3H, OCH_3), 4.89 (d, J=15.6 Hz, 1H, NCH), 5.10 (d, J=15.6 Hz, 1H, NCH), 6.85 (s, 1H, ArH), 6.88–6.92 (m, 2H, ArH), 7.12–7.17 (m, 4H, ArH), 7.19 (dd, J=8.5, 2.2 Hz, 1H, ArH), 7.23 (d, J=8.5 Hz, 1H, ArH), 7.46 (d, J=2.2 Hz, 1H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 16.1 (q), 42.1 (t), 51.8 (t), 55.5 (q), 109.2 (d), 124.5 (d), 126.4 (s), 126.8 (2× d), 127.0 (d), 127.1 (s), 127.4 (d), 128.4 (2× d), 129.3 (d), 129.9 (d), 130.8 (s), 133.8 (s), 136.3 (s), 137.2 (s), 138.6 (s), 158.9 (s), 170.8 (s); HMRS (EI) calcd for $C_{23}H_{20}ClNO_2$ m/e 377.1183, found m/e 377.1185.

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Supplementary data

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18. Crystal data for **9a**: $C_{21}H_{19}NO_4S$, M=381.44, T=200 (2) K, λ=0.71073 Å, monoclinic, space group C 2/c, a=29.5819(9) Å, b=8.8805(3) Å, c=14.8685(4) Å, α=90°, β=100.0250(10)°, γ=90°, V=3751.1(2) Å^3, Z=4, D_{calcd}=1.381 mg/m^3, μ=0.203 mm^{-1}, F (000)=1636, crystal size 0.54×0.45×0.11 mm^3, reflections collected 12,729, independent reflections 3300 [R (int)=0.0302], refinement method, full-matrix least-squares on F^2, goodness-of-fit on F^2 1.032, final R indices [$I>2\sigma$ (I)] R_1=0.0381, wR_2=0.0914, R indices (all data) R_1=0.0462, wR_2=0.0964, largest diff. peak and hole 0.378 and −0.321 e Å^{-3}. Crystallographic data for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 890808. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).
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