Regioselective Synthesis of Oxepin- and Oxocin-Annulated 2-Quinolones

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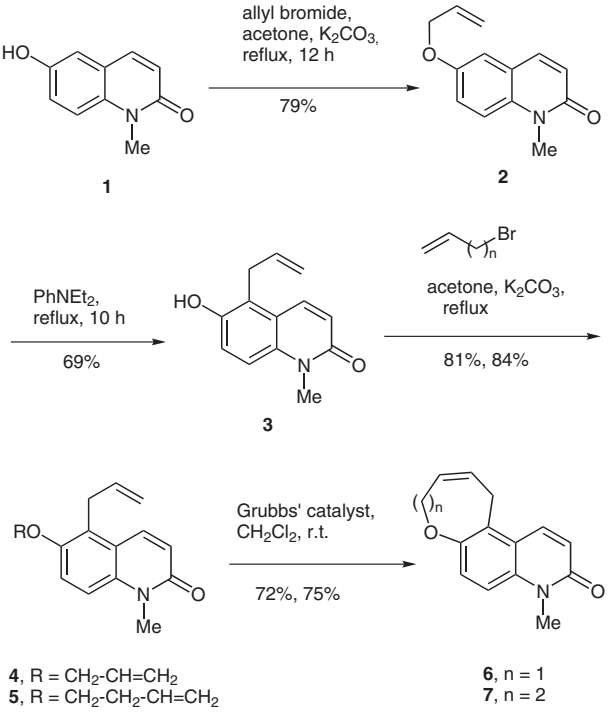
Abstract: A synthetic strategy based on tandem Claisen rearrangement and ring-closing metathesis was developed for the regioselective synthesis of some hitherto unknown oxepin- and oxocin-annulated 2-quinolones.

Key words: Claisen rearrangement, ring-closing metathesis, quinolones, oxepin, oxocin

Various quinolone derivatives are known[1] to display interesting biological properties ranging from microbial activity to cytotoxicity. For this and other reasons interest in the synthesis of new quinolone derivatives continues to increase.[2] Of particular interest have been[3] the furo- and pyranoquinolones because of their structural similarities with the photoactive furo- and pyranocoumarins. Other heterocyclic ring-fused quinolone derivatives have also been prepared. On the other hand, very little information is available about medium ring oxacycle-fused quinolone derivatives which may, in part, be due to lack of general methods for the synthesis of such ring systems.[4] In recent years ring-closing metathesis (RCM) has emerged[5,6] as a valuable tool for the construction of various carbocyclic and heterocyclic ring systems of varying size and complexity. Recently, we have described[7] a new methodology based on tandem Claisen rearrangement[8] and ring-closing metathesis reaction for the synthesis of oxepin- and oxocin-annulated coumarin derivatives and other systems of interest. Herein, we wish to report an analogous application of the said methodology for the synthesis of some hitherto unknown oxepin- and oxocin-fused quinolones.

Thus, starting from 6-hydroxy-*N*-methyl-2-quinolone[3c] (**1**), the corresponding allyl ether **2** (Scheme 1) was easily prepared by straightforward alkylation with allyl bromide. Claisen rearrangement of the allyl ether **2** in refluxing *N,N*-diethylaniline neatly provided the rearranged phenol **3** in good yield. Further alkylation of the latter with allyl bromide in refluxing acetone in the presence of anhydrous potassium carbonate afforded 5-allyl-6-allyloxy-*N*-methylquinolin-2-one (**4**) in high yield. Similarly, reaction of **3** with 4-bromobut-1-ene under analogous conditions provided the butenyl ether **5**. Ring-closing metathesis of the dienes **4** and **5** with the Grubbs' catalyst, bis(tricyclohexylphosphine)benzylideneruthenium(IV) dichloride, under our previously developed conditions[7a] neatly provided the



Scheme 1

angularly fused oxepinoquinolone **6** and the oxocinoquinolone **7**, respectively, in good yield.

On the other hand, attempted alkylation of 4-hydroxy-*N*-methylquinolone[9] (**8**) with allyl bromide under a range of conditions led only to the O,C-diallylated product **9** (Scheme 2) and the C,C- diallylated product **10** as a separable mixture. A similar observation has been made[10] in the alkylation of **8** with propargyl bromide. However, formation of **9** from **8** in a single step was an advantageous outcome since it could be directly utilized in the subsequent step. Ring-closing metathesis (RCM) of the O,C-diallylated product **9** smoothly provided the oxepinoquinolone derivative **11**. Similarly, the C,C-diallylated product **10** also underwent smooth RCM to give the spiroquinolone derivative **12** in good yield.

Several naturally occurring benzo-fused oxepin and oxocin derivatives have recently been found[11] to have interesting biological activities and therefore many synthetic studies[12] have been reported along this direction. The hitherto unknown quinolone-fused oxepin and oxocin derivatives reported here may prove to be of biological interest.

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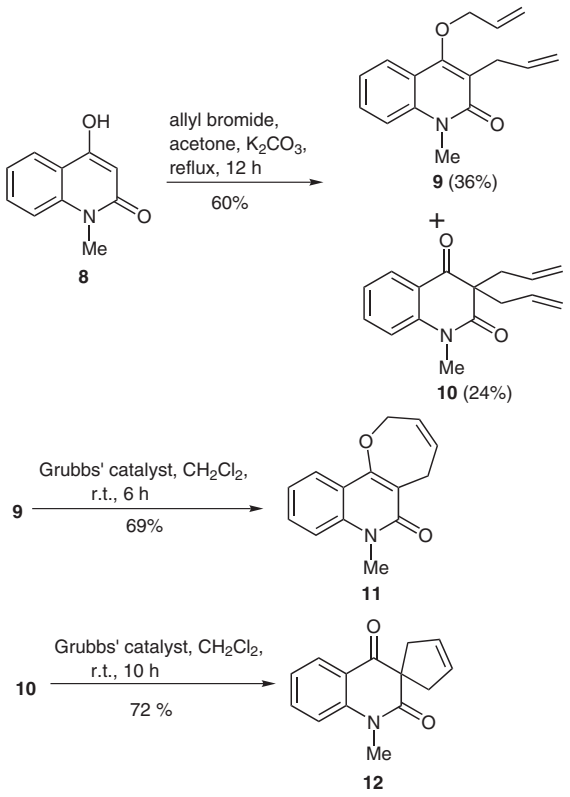

Scheme 2

Melting points were determined in open capillaries and are uncorrected. IR spectra were obtained on a Perkin Elmer 1600 FTIR spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX-300 spectrometer in $CDCl_3$ or DMSO-d_6 and referenced to the solvent signal. Low-resolution mass spectra were recorded on a JEOL-JMS 600 instrument at an ionizing potential of 70 eV. Microanalyses were performed on a Perkin-Elmer 204B elemental analyzer. Petroleum ether refers to the fraction boiling in the range 60–80 °C. Silica gel used was purchased from Spectrochem India Limited.

6-Allyloxy-*N*-methylquinolin-2-one (2)

A mixture of 6-hydroxy-*N*-methylquinoline-2-one (1.50 g, 8.56 mmol), anhyd K_2CO_3 (2.20 g, 15.9 mmol) and allyl bromide (2.21 g, 18.2 mmol) in anhyd acetone (30 mL) was refluxed under stirring for 12 h. The reaction mixture was then allowed to cool, filtered and the filtrate was concentrated in vacuo. The resulting mass was extracted with EtOAc (2 × 50 mL) and the organic extract was washed successively with 10% aq NaOH (2 × 25 mL), H_2O (25 mL) and brine (20 mL). It was then dried (Na_2SO_4), filtered and the filtrate was concentrated in vacuo to leave the crude product, which was purified by column chromatography (silica gel, 25% EtOAc in petroleum ether); colorless solid (1.44 g, 79%); mp 87–88 °C (EtOAc–petroleum ether).

IR (KBr): 1651, 1583, 1250, 854, 816 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.59 (d, 1 H, *J* = 9.5 Hz, H-4), 7.29 (d, 1 H, *J* = 9.2 Hz, H-8), 7.20 (dd, 1 H, *J* = 9.2, 2.7 Hz, H-7), 7.01 (d, 1 H, *J* = 2.7 Hz, H-5), 6.71 (d, 1 H, *J* = 9.5 Hz, H-3), 6.12–6.01 (m, 1 H, C*H*=CH$_2$), 5.44 (dd, 1 H, *J* = 17.3, 1.4 Hz, =C*H*$_2$), 5.32 (dd, 1 H, *J* = 10.5, 1.3 Hz, =C*H*$_2$), 4.6 (d, 2 H, *J* = 5.2 Hz, OCH$_2$), 3.7 (s, 3 H, NCH$_3$).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 161.7 (s, C-2), 153.5 (s, C-6), 138.4 (s, Ar), 138.2 (d, C-4), 134.5 (s, Ar), 132.8 (d, *C*H=CH$_2$), 122.1 (d, C-3), 119.6 (d, Ar), 117.8 (d, Ar), 115.3 (d, Ar), 111.5 (t, =CH$_2$), 69.1 (t, OCH$_2$), 29.3 (q, NCH$_3$).

Anal. Calcd for $C_{13}H_{13}NO_2$ (215.25): C, 72.54; H, 6.09; N, 6.51. Found: C, 72.22; H, 5.91; N, 6.33.

5-Allyl-6-hydroxy-*N*-methylquinolin-2-one (3)

A solution of the allyl ether **2** (1.15g, 5.34 mmol) in *N*,*N*-diethylaniline (8 mL) was refluxed for 10 h and then allowed to come to r.t. It was then poured into ice-cold 4 N HCl (20 mL) and the aqueous solution was then extracted with CH_2Cl_2 (2 × 50 mL). The combined organic extracts were washed successively with 5% aq $NaHCO_3$ solution (2 × 20 mL), H_2O (2 × 20 mL) and brine (20 mL). It was then dried (Na_2SO_4), filtered and the filtrate was concentrated in vacuo to leave the crude product which on chromatography (silica gel, EtOAc–petroleum ether, 1:1) provided the product **3** as a colorless solid (0.8 g, 69%); mp 232–234 °C (EtOH).

IR (KBr): 3462, 3058, 1646, 1579, 1566, 1404, 1297, 838, 808 cm^{-1}.

^{1}H NMR (300 MHz, DMSO-d_6): δ = 9.49 (s, 1 H, OH), 8.09 (d, 1 H, *J* = 9.1 Hz, H-4), 7.29 (d, 1 H, *J* = 8.6 Hz, H-8), 7.18 (d, 1 H, *J* = 8.7 Hz, H-7), 6.57 (d, 1 H, *J* = 9.3 Hz, H-3), 5.95–5.90 (m, 1 H, C*H*=CH$_2$), 4.97–4.86 (m, 2 H, CH=C*H*$_2$), 3.63–3.57 (overlapped, 5 H, NCH$_3$ + C*H*$_2$CH=CH$_2$).

Anal. Calcd for $C_{13}H_{13}NO_2$ (215.25): C, 72.54; H, 6.09; N, 6.51. Found: C, 72.31; H, 5.86; N, 6.28.

5-Allyl-6-allyloxy-*N*-methylquinolin-2-one (4)

A mixture of the phenol **3** (0.25 g, 1.16 mmol), anhyd K_2CO_3 (0.30g, 2.14 mmol) and allyl bromide (0.3 g, 2.5 mmol) in anhyd acetone (5 mL) was refluxed under stirring for 12 h. The reaction mixture was then allowed to cool, filtered and the filtrate was concentrated in vacuo. The resulting mass was extracted with EtOAc (2 × 20 mL) and the combined organic extracts were washed successively with 10% aq NaOH (2 × 10 mL), H_2O (20 mL) and brine (20 mL). It was then dried (Na_2SO_4), filtered and the filtrate was concentrated in vacuo to leave the crude product which on chromatography (silica gel, EtOAc–petroleum ether, 1:3) provided the product **4** as a colorless solid (0.24 g, 81%); mp 53–54 °C (petroleum ether).

IR (KBr): 1655, 1614, 1584, 1569, 1456, 1267, 984, 833 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.87 (d, 1 H, *J* = 9.8 Hz, H-4), 7.26–7.18 (m, 2 H, Ar-H), 6.73 (d, 1 H, *J* = 9.8 Hz, H-3), 6.11–5.91 (m, 2 H, 2 × C*H*=CH$_2$), 5.42 (d, 1 H, *J* = 17.3 Hz, =CH$_2$), 5.28 (dd, 1 H, *J* = 10.5, 1.0 Hz, =CH$_2$), 5.03 (d, 1 H, *J* = 10.0 Hz, =CH$_2$), 4.92 (d, 1 H, *J* = 17.1 Hz, =CH$_2$), 4.61–4.59 (m, 2 H, OCH$_2$), 3.75 (d, 2 H, *J* = 5.6 Hz, 5-CH$_2$), 3.71(s, 3 H, NCH$_3$).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 161.5 (s, C-2), 151.1 (s, C-6), 136.5 (d, C-4), 135.6 (d, *C*H=CH$_2$), 135.3 (s, Ar), 133.2 (d, *C*H=CH$_2$), 125.2 (s, Ar), 121.8 (d, C-3), 120.2 (s, Ar), 117.2 (d, Ar), 116.5 (t, =CH$_2$), 115.6 (d, Ar), 113.0 (t, =CH$_2$), 70.0 (t, OCH$_2$), 29.5 (q, NCH$_3$), 29.0 (t, Ar*C*H$_2$).

Anal. Calcd for $C_{16}H_{17}NO_2$ (255.32): C, 75.27; H, 6.71; N, 5.48. Found: C, 74.91; H, 6.46; N, 5.29.

5-Allylbut-6-enyloxy-*N*-methylquinolin-2-one (5)

A mixture of the phenol **3** (0.25 g, 1.16 mmol), anhyd K_2CO_3 (0.40 g, 2.80 mmol) and 4-bromobut-1-ene (0.53 g, 3.9 mmol) in anhyd acetone (10 mL) was refluxed under stirring for 20 h. The reaction mixture was then allowed to cool, filtered and the filtrate was concentrated in vacuo. The resulting mass was extracted with EtOAc (2 × 20 mL) and the combined organic extracts were washed successively with 10% aq NaOH (2 × 10 mL), H_2O (20 mL) and brine (20 mL). It was then dried (Na_2SO_4), filtered and the filtrate was concentrated in vacuo to leave the crude product which on chroma-

tography (silica gel, EtOAc–petroleum ether, 1:3) provided the product **5** as a colorless solid (0.21 g, 84%); mp 65–66 °C (EtOAc–petroleum ether).

IR (KBr): 1658, 1615, 1585, 1570, 1456, 1269 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.92 (d, 1 H, *J* = 9.91 Hz, H-4), 7.34–7.28 (m, 2 H, ArH), 6.94 (d, 1 H, *J* = 9.80 Hz, H-3), 6.10–5.88 (m, 2 H, 2 × C*H*=CH_2), 5.46 (d, 1 H, *J* = 17.41 Hz, =CH_2), 5.20–5.12 (m, 2 H, =CH_2), 4.92 (dd, 1 H, *J* = 1.3, 17.1 Hz, =CH_2), 4.45 (t, 2 H, *J* = 6.6 Hz, OCH_2), 3.79 (d, 2 H, *J* = 5.8 Hz, ArCH_2), 3.70 (s, 3 H, NCH_3), 2.59–2.51 (m, 2 H, OCH_2CH_2).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.0 (s, C-2), 151.9 (s, C-6), 136.5 (d, C-4), 135.6 (d, *C*H=CH_2), 135.4 (s, Ar), 134.8 (d, *C*H=CH_2), 125.7 (s, Ar), 122.3 (d, C-3), 120.7 (s, Ar), 117.5 (d, Ar), 116.6 (t, =CH_2), 115.9 (t, =CH_2), 113.5 (d, Ar), 69.1 (t, OCH_2), 34.3 (t, OCCH_2), 30.0 (q, NCH_3), 29.5 (t, 5-CH_2).

Anal. Calcd for $C_{17}H_{19}NO_2$ (269.34): C, 75.81; H, 7.11; N, 5.20. Found: C, 75.59; H, 6.96; N, 5.39.

3-Allyl-4-allyloxy-*N*-methylquinolin-2-one (9) and 3,3-Diallyl-1-methylquinoline-2,4-(1*H*,3*H*)-dione (10)

A mixture of 4-hydroxy-*N*-methylquinoline-2-one[13] (0.34 g, 1.94 mmol), anhyd K_2CO_3 (0.51 g, 3.6 mmol) and allyl bromide (0.51 g, 4.12 mmol) in anhyd acetone (10 mL) was refluxed under stirring for 12 h. The reaction mixture was then allowed to cool, filtered and the filtrate was concentrated in vacuo. The resulting mass was extracted with EtOAc (2 × 50 mL) and the combined organic extracts were washed successively with 10% aq NaOH (10%, 2 × 25 mL), H_2O (25 mL) and brine (20 mL). It was then dried (Na_2SO_4), filtered and the filtrate was concentrated in vacuo to leave the crude product which on flash chromatography over silica gel (petroleum ether) provided the C,C-diallylated product **10** as a viscous liquid (0.12 g, 24%).

10

IR (neat): 1694, 1659, 1602, 1473, 1362, 1302, 924, 763 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.01 (d, 1 H, *J* = 7.8 Hz, H-5), 7.62 (dt, 1 H, *J* = 1.4, 8.1 Hz, H-6/7), 7.19–7.13 (m, 2 H, Ar-H), 5.60–5.46 (m, 2 H, 2 × C*H*=CH_2), 5.02 (d, 2 H, *J* = 17 Hz, =CH_2), 4.92 (d, 2 H, *J* = 10.1 Hz, =CH_2), 3.46 (s, 3 H, NCH_3), 2.80–2.68 (m, 4 H, 2 × CH_2CH=CH_2).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 196.3 (s, C-4), 172.0 (s, C-2), 143.2 (s, Ar), 136.1 (d, Ar), 131.9 (d, *C*H=CH_2), 127.5 (d, Ar), 122.9 (d, Ar), 120.7 (s, Ar), 118.9 (t, CH=*C*H_2), 114.7 (d, Ar), 61.4 (s, C-3), 42.8 (t, *C*H_2CH=CH_2), 29.3 (q, NCH_3).

Anal. Calcd for $C_{16}H_{17}NO_2$ (255.32): C, 75.27; H, 6.71; N, 5.49. Found: C, 74.94; H, 6.49; N, 5.20.

Further elution with 5% EtOAc in petroleum ether provided the O,C-diallylated product **9** as a viscous liquid (0.18 g, 36%).

9

IR (neat): 1640, 1596, 1464, 1232, 756 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.84 (d, 1 H, *J* = 7.9 Hz, H-5), 7.56 (t, 1 H, *J* = 7.6 Hz, H-6/7), 7.37 (d, 1 H, *J* = 8.5 Hz, H-8), 7.26 (t, 1 H, *J* = 9.1 Hz, H-6/7), 6.21–5.98 (m, 2 H, 2 × C*H*=CH_2), 5.49 (d, 1 H, *J* = 17.1 Hz, =CH_2), 5.33 (d, 1 H, *J* = 10.4 Hz, =CH_2), 5.10 (d, 1 H, *J* = 16.9 Hz, =CH_2), 5.03 (d, 1 H, *J* = 9.8 Hz, =CH_2), 4.54 (d, 2 H, *J* = 5.4 Hz, OCH_2), 3.74 (s, 3 H, NCH_3), 3.47–3.32 (m, 2 H, 3-CH_2).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.6 (s, C-2), 159.7 (s, C-4), 139.1 (d, *C*H=CH_2), 135.7 (d, *C*H=CH_2), 132.9 (s, Ar), 132.0 (d, Ar), 130.3 (d, Ar), 123.6 (d, Ar), 121.9 (d, Ar), 119.1 (s, C-3), 118.0 (s, Ar), 115.4 (t, =CH_2), 114.1 (t, =CH_2), 75.1 (t, OCH_2), 29.7 (q, NCH_3), 29.6 (t, 3-CH_2).

Anal. Calcd for $C_{16}H_{17}NO_2$ (255.32): C, 75.27; H, 6.71; N, 5.49. Found: C, 75.44; H, 6.89; N, 5.31.

Ring-Closing Metathesis; General Procedure

A solution of the appropriate diene **4**,**5**,**9** or **10** (0.2 mmol) and Grubbs' catalyst (5 mol%) in anhyd and degassed CH_2Cl_2 (25 mL) was stirred under argon at r.t. until the starting material was consumed (6–24 h). The reaction mixture was then concentrated and chromatographed.

4-Methyl-3,4,8,11-tetrahydrooxepino[3,2-*f*]quinolin-3-one (6)

The reaction was complete in 18 h. The product was eluted with 30% EtOAc in petroleum ether; yield: 72%: mp 147–149 °C (EtOAc–petroleum ether).

IR (KBr): 1651, 1586, 1457, 1241, 1057, 829, 632 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.96 (d, 1 H, *J* = 9.9 Hz, H-1), 7.34 (d, 1 H, *J* = 9.1 Hz, H-5), 7.22 (d, 1 H, *J* = 9.0 Hz, H-6), 6.77 (d, 1 H, *J* = 9.9 Hz, H-2), 5.92–5.87 (m, 1 H, H-9), 5.49 (d, 1 H, *J* = 10.8 Hz, H-10), 4.62 (s, 2 H, H-8), 3.76 (s, 2 H, H-11), 3.72 (s, 3 H, NCH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 161.6 (s, C-3), 153.3 (s, OC_{arom}), 137.2 (s, Ar), 134.4 (s, Ar), 134.2 (d, C-1), 128.1 (d, C-9), 124.7 (d, C-10), 124.5 (d, Ar), 121.6 (d, C-2), 118.1 (s, Ar), 113.3 (d, Ar), 71.4 (t, C-8), 29.8 (q, NCH_3), 24.4 (t, C-11).

MS (EI): *m*/*z* (%) = 227 (42), 212 (100).

Anal. Calcd for $C_{14}H_{13}NO_2$ (227.26): C, 73.99; H, 5.76; N, 6.16. Found: C, 73.71; H, 5.49; N, 6.34.

4-Methyl-3,8,9,12-tetrahydro-4*H*-oxocino[3,2-*f*]quinolin-3-one (7)

The reaction was complete in 24 h. The product was eluted with 25% EtOAc in petroleum ether and was obtained as a viscous liquid; yield: 75%.

IR (neat): 1659, 1595, 1440, 1345, 780 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.96 (d, 1 H, *J* = 9.9 Hz, H-1), 7.34 (d, 1 H, *J* = 9.1 Hz, H-5), 7.31 (d, 1 H, *J* = 9.3 Hz, H-6), 6.77(d, 1 H, *J* = 9.9 Hz, H-2), 6.04–5.89 (m, 1 H, H-11), 5.71–5.63 (m, 1 H, H-10), 4.05 (t, 2 H, *J* = 4.4 Hz, H-8), 3.72 (s, 5 H, NCH_3 + H-12), 2.61–2.56 (m, 2 H, H-9).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.8 (s, C-3), 154.0 (s, OC_{arom}), 138.2 (s, Ar), 135.8 (d, C-1), 132.4 (d, C-10), 128.8 (d, C-11), 126.0 (s, NC_{arom}), 125.8 (d, C-2), 121.7 (d, Ar), 121.2 (s), 113.2 (d, Ar), 72.2 (t, C-8), 33.4 (t, C-9), 29.6 (q, NCH_3), 25.6(t, C-12).

MS (EI): *m*/*z* (%) = 241 (100), 213 (16.7), 187 (22.8).

Anal. Calcd for $C_{15}H_{15}NO_2$ (241.29): C, 74.67; H, 6.26; N, 5.80. Found: C, 74.79; H, 6.40; N, 6.04.

7-Methyl-2,5,6,7-tetrahydrooxepino[3,2-*c*]quinolin-6-one (11)

The reaction was complete in 6 h. The product was eluted with 5% EtOAc in petroleum ether and was obtained as a colorless solid; yield: 69%; mp 118–119 °C (EtOAc–petroleum ether).

IR (KBr): 1652, 1601, 1473, 1355, 779 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.94 (d, 1 H, *J* = 7.9 Hz, H-8), 7.59–7.51 (m, 1 H, H-11), 7.33–7.29 (m, 1 H, H-10), 7.25–7.20 (m, 1 H, H-9), 6.14–6.07 (m, 1 H, H-3), 5.92–5.85 (m, 1 H, H-4), 4.82 (d, 2 H, *J* = 4.7, H-2), 3.81 (overlapped 5 H, NCH_3 + CH_2C=C).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.2 (s, C-6), 159.4 (s, O*C*=C), 138.6 (s, Ar), 131.4 (d, C-3), 130.1 (d, C-4), 126.6 (d, Ar), 126.3 (d, Ar), 124.4 (d, Ar), 123.6 (d, Ar), 122.1 (s, OC=*C*), 119.1 (s, Ar), 71.1 (t, C-2), 29.7 (q, NCH_3), 25.2 (t, C-5).

MS (EI): *m*/*z* (%) = 227 (86), 212 (41), 175 (31), 147 (100).

Anal. Calcd for $C_{14}H_{13}NO_2$ (227.26): C, 73.99; H, 5.76; N, 6.16. Found: C, 74.28; H, 5.92; N, 6.31.

Compound 12

The reaction was complete in 10 h. The product was eluted with 10% EtOAc in petroleum ether and was obtained as a colorless solid; yield: 72%; mp 119–120 °C (CH_2Cl_2–petroleum ether).

IR (KBr): 1690, 1652, 1601, 1472, 1416, 1354, 780 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.99 (dd, 1 H, *J* = 6.6, 1.5 Hz, H-5), 7.64 (dt, 1 H, *J* = 7.5, 1.7 Hz, H-6/7), 7.21–7.16 (m, 2 H, Ar), 5.64 (s, 2 H, CH=CH), 3.48 (s, 3 H, NCH_3), 3.02 (s, 4 H, CH_2C=C).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 195.4 (s, C-4), 173.7 (s, C-2), 143.3 (s, Ar), 135.7 (d, Ar), 128.3 (d, CH=CH), 127.2 (d, Ar), 123.0 (d, Ar), 120.3 (s, Ar), 114.8 (d, Ar), 61.6 (s, C-3), 42.9 (t, *C*H_2C=C), 30.0 (q, NCH_3).

MS (EI): *m*/*z* (%) = 227 (100), 212 (49), 198 (42).

Anal. Calcd for $C_{14}H_{13}NO_2$ (227.26): C, 73.99; H, 5.76; N, 6.16. Found: C, 74.17; H, 5.88; N, 6.27.

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