# Introduction of a clean and promising protocol for the synthesis of β-amino acrylates and 1,4-benzoheterocycles: An emerging innovation

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***Supplementary Information (File-1)***

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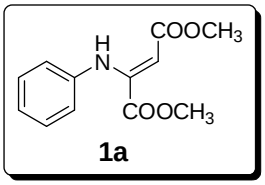
***Dimethyl N-(phenyl)aminofumarate* (1a)**



**1a**

Yellow viscous liquid.

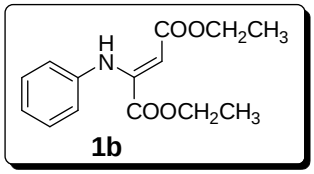
**IR (KBr):** $\nu_{max}$ 3283 (NH), 1739 (C=O), 1672 (C=O), 1605 (C=C), 1281 (C-O) $cm^{-1}$.

**$^1$H NMR (500 MHz, $CDCl_3$):** δ 9.67 (br s, 1H, NH), 7.64 (d, *J* = 7.5 Hz, 1H, benzene hydrogen), 7.39 (t, *J* = 7.5 Hz, 1H, benzene CH), 7.29 (d, *J* = 8.0 Hz, 1H, benzene CH), 7.09 (t, *J* = 7.5 Hz, 1H, benzene CH), 6.85 (t, *J* = 7.5 Hz, 1H, benzene CH), 5.39 (s, 1H, CH), 3.83 (s, 3H, $CH_3$), 3.70 (s, 3H, $CH_3$) ppm.

**$^{13}$C NMR (125 MHz, $CDCl_3$):** δ 169.5 (CO), 164.7 (CO), 147.9 (C), 141.1 (C), 124.2 (benzene CH), 120.6 (benzene CH), 118.7 (benzene CH), 93.5 (CH), 52.1 ($CH_3$), 52.0 ($CH_3$) ppm.

**MS (EI, 70 eV):** *m*/*z* 235 [$M^+$].

***Diethyl N-(phenyl)aminofumarate (1b)***



**1b**

Yellow viscous liquid.

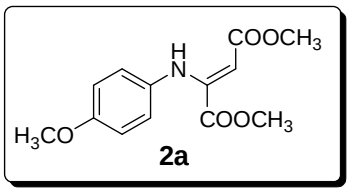
**IR (KBr):** $\nu_{max}$ 3286, 1738, 1667, 1597, 1275 $cm^{-1}$.

**$^1$H NMR (500 MHz, $CDCl_3$):** δ 9.69 (br s, 1H), 7.32-7.26 (m, 2H), 7.11 (t, *J* = 7.5 Hz, 1H), 6.94 (d, *J* = 8.0 Hz, 2H), 5.40 (s, 1H), 4.22 (q, *J* = 7.0 Hz, 2H), 4.17 (q, *J* = 7.5 Hz, 2H), 1.33 (t, *J* = 7.0 Hz, 3H), 1.11 (t, *J* = 7.0 Hz, 3H) ppm.

**$^{13}$C NMR (125 MHz, $CDCl_3$):** δ 169.6, 164.4, 148.4, 140.4, 129.0, 124.2, 121.0, 93.8, 62.0, 60.0, 14.3, 13.6 ppm.

**MS (EI, 70 eV):** *m*/*z* 263 [$M^+$].

***Dimethyl N-(4-methoxyphenyl)aminofumarate (2a)***



**2a**

Yellow solid, **m.p.:** 68–70 °C.

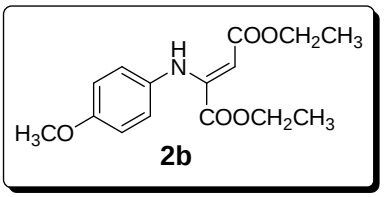
**IR (KBr):** $\nu_{max}$ 3284, 1739, 1669, 1611, 1291 $cm^{-1}$.

**$^1$H NMR (500 MHz, $CDCl_3$):** δ 9.58 (br s, 1H), 6.90-6.86 (m, 2H), 6.84-6.81 (m, 2H), 5.30 (s, 1H), 3.78 (s, 3H), 3.74 (s, 3H), 3.67 (s, 3H) ppm.

**$^{13}$C NMR (125 MHz, $CDCl_3$):** δ 170.0, 164.8, 156.8, 149.0, 133.3, 122.9, 114.3, 91.6, 55.4, 52.6, 51.0 ppm.

**MS (EI, 70 eV):** *m*/*z* 265 [$M^+$].

***Diethyl N-(4-methoxyphenyl)aminofumarate (2b)***




Yellow viscous liquid.

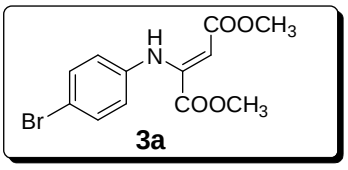
**IR (KBr):** $\nu_{max}$ 3285, 1737, 1665, 1612, 1274 $cm^{-1}$.

**$^{1}$H NMR (500 MHz, $CDCl_3$):** δ 9.57 (br s, 1H), 6.91-6.88 (m, 2H), 6.84-6.80 (m, 2H), 5.29 (s, 1H), 4.19 (q, *J* = 7.0 Hz, 2H), 4.13 (q, *J* = 7.0 Hz, 2H), 3.78 (s, 3H), 1.30 (t, *J* = 7.0 Hz, 3H), 1.09 (t, *J* = 7.0 Hz, 3H) ppm.

**$^{13}$C NMR (125 MHz, $CDCl_3$):** δ 169.8, 164.4, 156.9, 149.4, 133.5, 123.3, 114.3, 91.9, 61.9, 59.8, 55.4, 14.4, 13.7 ppm.

**MS (EI, 70 eV):** *m*/*z* 293 [$M^+$].

***Dimethyl N-(4-bromophenyl)aminofumarate (3a)***




Yellow solid, **m.p.:** 80-81 $^{o}$C (Lit. 83-86 $^{o}$C)[31].

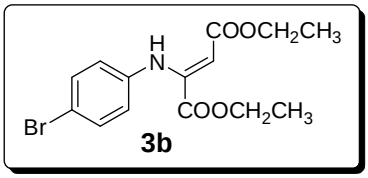
**IR (KBr):** $\nu_{max}$ 3278, 1739, 1672, 1617, 1281 $cm^{-1}$.

**$^{1}$H NMR (500 MHz, $CDCl_3$):** δ 9.60 (br s, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 6.76 (d, *J* = 9.0 Hz, 2H), 5.45 (s, 1H), 3.75 (s, 3H), 3.72 (s, 3H) ppm.

**$^{13}$C NMR (125 MHz, $CDCl_3$):** δ 169.7, 164.4, 147.2, 139.4, 132.1, 131.9 122.2, 117.0, 116.9, 94.8, 52.9, 51.3 ppm.

**MS (EI, 70 eV):** *m*/*z* 313 [$M^+$].

***Diethyl N-(4-bromophenyl)aminofumarate (3b)***




Yellow viscous liquid.

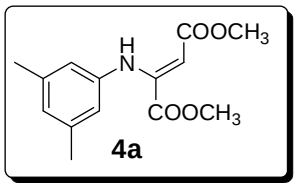
**IR (KBr):** $\nu_{max}$ 3284, 1736, 1668, 1616, 1276 $cm^{-1}$.

**$^{1}$H NMR (500 MHz, $CDCl_3$):** δ 9.60 (br s, 1H), 7.37 (d, *J* = 5.0 Hz, 2H), 6.79 (d, *J* = 5.0 Hz, 2H), 5.44 (s, 1H), 4.21-4.15 (m, 4H), 1.30 (t, *J* = 7.0 Hz, 3H), 1.15 (t, *J* = 7.0 Hz, 3H) ppm.

**$^{13}$C NMR (125 MHz, $CDCl_3$):** δ 169.4, 164.0, 147.7, 139.6, 132.0, 122.5, 117.0, 95.0, 62.2, 60.1, 14.3, 13.7 ppm.

**MS (EI, 70 eV):** *m*/*z* 341 [$M^+$].

***Dimethyl N-(3,5-dimethylphenyl)aminofumarate (4a)***




Yellow solid, **m.p.:** 59-61 $^{o}$C.

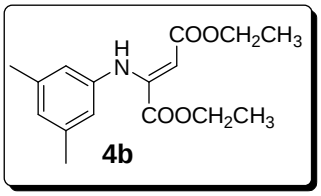
**IR (KBr):** $\nu_{max}$ 3285, 1741, 1671, 1599, 1281 cm$^{-1}$.

**$^{1}$H NMR (500 MHz, CDCl$_3$):** δ 9.58 (br s, 1H), 6.73 (s, 1H), 6.52 (s, 2H), 5.33 (s, 1H), 3.73 (s, 3H), 3.70 (s, 3H), 2.26 (s, 6H) ppm.

**$^{13}$C NMR (125 MHz, CDCl$_3$):** δ 169.8, 165.0, 148.1, 140.0, 138.8, 126.0, 118.3, 92.8, 52.6, 51.1, 21.2 ppm.

**MS (EI, 70 eV):** *m*/*z* 263 [M$^{+}$].

***Diethyl N-(3,5-dimethylphenyl)aminofumarate (4b)***




Yellow viscous liquid.

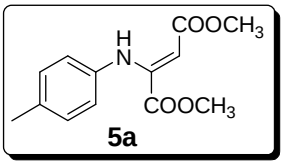
**IR (KBr):** $\nu_{max}$ 3284, 1737, 1667, 1599, 1278 cm$^{-1}$.

**$^{1}$H NMR (500 MHz, CDCl$_3$):** δ 9.58 (br s, 1H), 6.79 (s, 2H), 6.72 (s, 1H), 5.32 (s, 1H), 4.37 (q, *J* = 7.0 Hz, 2H), 4.12 (q, *J* = 7.5 Hz, 2H), 2.29 (s, 6H), 1.37 (t, *J* = 7.0 Hz, 3H), 1.24 (t, *J* = 6.5 Hz, 3H) ppm.

**$^{13}$C NMR (125 MHz, CDCl$_3$):** δ 169.6, 164.6, 148.7, 140.1, 138.7, 126.0, 118.8, 93.1, 62.0, 59.9, 21.2, 14.4, 13.7 ppm.

**MS (EI, 70 eV):** *m*/*z* 291 [M$^{+}$].

***Dimethyl N-(4-methylphenyl)aminofumarate (5a)***




Yellow solid, **m.p.:** 71-73 $^{o}$C (Lit. 89-91 $^{o}$C)[32].

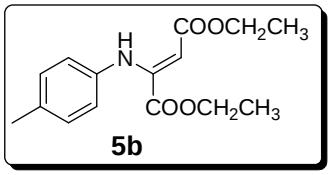
**IR (KBr):** $\nu_{max}$ 3290, 1742, 1675, 1609, 1282 cm$^{-1}$.

**$^{1}$H NMR (500 MHz, CDCl$_3$):** δ 9.62 (br s, 1H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.80 (d, *J* = 8.5 Hz, 2H), 5.33 (s, 3H), 3.73 (s, 3H), 3.69 (s, 3H), 2.30 (s, 3H) ppm.

**$^{13}$C NMR (125 MHz, CDCl$_3$):** δ 170.0, 164.9, 148.4, 137.7, 134.1, 129.9, 120.9, 92.5, 52.8, 51.1, 20.8 ppm.

**MS (EI, 70 eV):** *m*/*z* 249 [M$^{+}$].

***Diethyl N-(4-methylphenyl)aminofumarate (5b)***




Yellow viscous liquid.

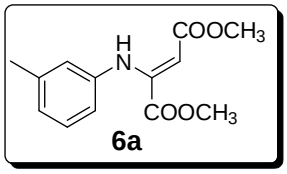
**IR (KBr):** $\nu_{max}$ 3284, 1737, 1667, 1610, 1275 $cm^{-1}$.

**$^1$H NMR (500 MHz, $CDCl_3$):** δ 9.62 (br s, 1H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.82 (d, *J* = 8.5 Hz, 2H), 5.32 (s, 1H), 4.19 (q, *J* = 7.0 Hz, 2H), 4.15 (q, *J* = 6.5 Hz, 2H), 2.30 (s, 3H), 1.30 (t, *J* = 7.0 Hz, 3H), 1.11 (t, *J* = 7.5 Hz, 3H) ppm.

**$^{13}$C NMR (125 MHz, $CDCl_3$):** δ 169.7, 164.4, 148.9, 137.8, 134.0, 129.6, 121.2, 92.7, 62.0, 59.8, 20.8, 14.1, 13.7 ppm.

**MS (EI, 70 eV):** *m*/*z* 277 [$M^+$].

***Dimethyl N-(3-methylphenyl)aminofumarate (6a)***



**6a**

Yellow solid, **m.p.:** 65-66 °C.

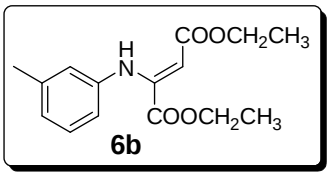
**IR (KBr):** $\nu_{max}$ 3459, 1741, 1681, 1601, 1273 $cm^{-1}$.

**$^1$H NMR (500 MHz, $CDCl_3$):** δ 9.62 (br s, 1H), 7.16 (t, *J* = 7.5 Hz, 1H), 6.90 (d, *J* = 7.5 Hz, 1H), 6.73 (s, 1H), 6.68 (dd, *J* = 1.5, 8.0 Hz, 1H), 5.36 (s, 1H), 3.74 (s, 3H), 3.70 (s, 3H), 2.31 (s, 3H) ppm.

**$^{13}$C NMR (125 MHz, $CDCl_3$):** δ 169.9, 165.0, 148.1, 140.2, 139.1, 128.9, 125.1, 121.4, 117.7, 93.2, 52.8, 51.2, 21.4 ppm.

**MS (EI, 70 eV):** *m*/*z* 249 [$M^+$].

***Diethyl N-(3-methylphenyl)aminofumarate (6b)***



**6b**

Yellow viscous liquid.

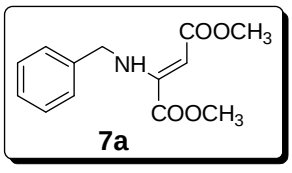
**IR (KBr):** $\nu_{max}$ 3282, 1735, 1668, 1609, 1280 $cm^{-1}$.

**$^1$H NMR (500 MHz, $CDCl_3$):** δ 9.63 (br s, 1H), 7.15 (t, *J* = 7.5 Hz, 1H), 6.90 (d, *J* = 7.5 Hz, 1H), 6.74 (s, 1H), 6.71 (d, *J* = 8.0 Hz, 1H), 5.35 (s, 1H), 4.19 (q, *J* = 7.0 Hz, 2H), 4.16 (q, *J* = 7.0 Hz, 2H), 2.30 (s, 3H), 1.30 (t, *J* = 7.0 Hz, 3H), 1.11 (t, *J* = 7.5 Hz, 3H) ppm.

**$^{13}$C NMR (125 MHz, $CDCl_3$):** δ 169.6, 164.5, 148.6, 140.3, 139.0, 128.9, 125.1, 121.7, 118.0, 93.4, 62.0, 59.9, 21.3, 14.1, 13.7 ppm.

**MS (EI, 70 eV):** *m*/*z* 277 [$M^+$].

***Dimethyl 2-(benzylamino)fumarate (7a)***



**7a**

Yellow viscous liquid.

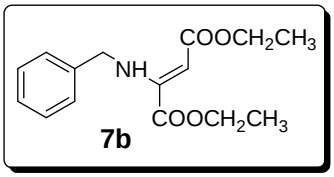
**IR (KBr):** $\nu_{max}$ 3312, 1745, 1677, 1591, 1269 $cm^{-1}$.

**$^1$H NMR (500 MHz, $CDCl_3$):** δ 8.42 (br s, 1H), 7.36-7.33 (m, 3H), 7.31-7.28 (m, 2H), 5.20 (s, 1H), 4.58 (d, *J* = 6.5 Hz, 2H), 3.80 (s, 3H), 3.70 (s, 3H) ppm.

**$^{13}$C NMR (125 MHz, $CDCl_3$):** δ 170.5, 164.1, 151.4, 138.8, 128.7, 127.5, 127.3, 88.0, 52.7, 50.8, 48.6 ppm.

**MS (EI, 70 eV):** *m*/*z* 249 [$M^+$].

***Diethyl 2-(benzylamino)fumarate (7b)***




Yellow viscous liquid.

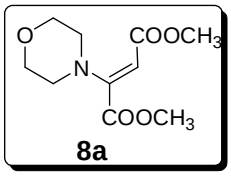
**IR (KBr):** $\nu_{max}$ 3305, 1734, 1662, 1606, 1289 $cm^{-1}$.

**$^1$H NMR (500 MHz, $CDCl_3$):** δ 8.42 (br s, 1H), 7.37-7.32 (m, 3H), 7.31-7.28 (m, 2H), 5.18 (s, 1H), 4.58 (d, *J* = 6.5 Hz, 2H), 4.24 (q, *J* = 7.5 Hz, 2H), 4.14-4.18 (m, 2H), 1.26-1.30 (m, 6H) ppm.

**$^{13}$C NMR (125 MHz, $CDCl_3$):** δ 170.2, 163.7, 151.6, 138.9, 128.7, 127.4, 127.3, 88.2, 61.9, 59.4, 48.5, 14.4, 13.9 ppm.

**MS (EI, 70 eV):** *m*/*z* 277 [$M^+$].

***Dimethyl 2-morpholinofumarate (8a)***




Yellow viscous liquid.

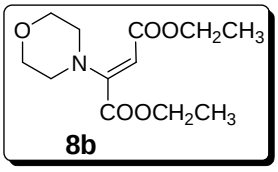
**IR (KBr):** $\nu_{max}$ 1742, 1695, 1584, 1275 $cm^{-1}$.

**$^1$H NMR (500 MHz, $CDCl_3$):** δ 4.80 (s, 1H), 3.93 (s, 3H), 3.75 (t, *J* = 5.0 Hz, 4H), 3.65 (s, 3H), 3.14 (t, *J* = 5.0 Hz, 4H) ppm.

**$^{13}$C NMR (125 MHz, $CDCl_3$):** δ 167.7, 165.7, 154.6, 87.0, 65.7, 52.9, 50.9, 47.0 ppm.

**MS (EI, 70 eV):** *m*/*z* 229 [$M^+$].

***Diethyl 2-morpholinofumarate (8b)***




Yellow viscous liquid.

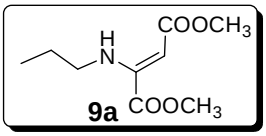
**IR (KBr):** $\nu_{max}$ 1739, 1693, 1584, 1275 $cm^{-1}$.

**$^1$H NMR (500 MHz, $CDCl_3$):** δ 4.81 (s, 1H), 4.40 (q, *J* = 7.5 Hz, 2H), 4.13 (q, *J* = 7.0 Hz, 2H), 3.76 (t, *J* = 5.0 Hz, 4H), 3.16 (t, *J* = 5.0 Hz, 4H), 1.39 (t, *J* = 7.0 Hz, 3H), 1.26 (t, *J* = 7.0 Hz, 3H) ppm.

**$^{13}$C NMR (125 MHz, $CDCl_3$):** δ 167.2, 165.4, 154.7, 87.6, 65.9, 62.2, 59.5, 47.0, 14.4, 13.9 ppm.

**MS (EI, 70 eV):** *m*/*z* 257 [$M^+$].

***Dimethyl 2-(propylamino)fumarate (9a)***



**9a**

Yellow viscous liquid.

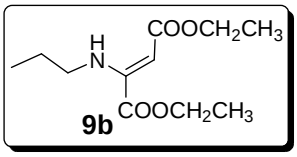
**IR (KBr):** $\nu_{max}$ 3303, 1740, 1664, 1609, 1283 $cm^{-1}$.

**$^1$H NMR (500 MHz, $CDCl_3$):** δ 8.11 (br s, 1H), 5.05 (s, 1H), 3.84 (s, 3H), 3.68 (s, 3H), 3.29 (q, *J* = 7.0 Hz, 2H), 1.61-1.55 (m, 2H), 0.95 (t, *J* = 7.0 Hz, 3H) ppm.

**$^{13}$C NMR (125 MHz, $CDCl_3$):** δ 172.0, 164.3, 151.8, 84.2, 52.9, 50.7, 45.3, 21.2, 11.3 ppm.

**MS (EI, 70 eV):** *m*/*z* 201 [$M^+$].

***Diethyl 2-(propylamino)fumarate (9b)***



**9b**

Yellow viscous liquid.

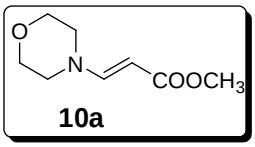
**IR (KBr):** $\nu_{max}$ 3305, 1734, 1662, 1606, 1289 $cm^{-1}$.

**$^1$H NMR (500 MHz, $CDCl_3$):** δ 8.12 (br s, 1H), 5.03 (s, 1H), 4.29 (q, *J* = 7.0 Hz, 2H), 4.13 (q, *J* = 7.0 Hz, 2H), 3.29 (q, *J* = 6.5 Hz, 2H), 1.62-1.54 (m, 2H), 1.34 (t, *J* = 7.0 Hz, 3H), 1.27 (t, *J* = 7.0 Hz, 3H), 0.95 (t, *J* = 7.5 Hz, 3H) ppm.

**$^{13}$C NMR (125 MHz, $CDCl_3$):** δ 170.2, 163.7, 152.2, 86.2, 60.8, 59.1, 46.4, 24.0, 14.2, 11.0 ppm.

**MS (EI, 70 eV):** *m*/*z* 229 [$M^+$].

***Methyl (E)-3-morpholinoacrylate (10a)***



**10a**

White solid, **m.p.:** 73-74 $^oC$ (Lit. 72-74 $^oC$)[33].

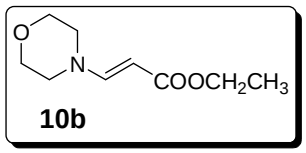
**IR (KBr):** $\nu_{max}$ 1699 (C=O), 1641 (C=C), 1239 (C-O), 973 (*trans* hydrogens) $cm^{-1}$.

**$^1$H NMR (500 MHz, $CDCl_3$):** δ 7.35 (d, *J* = 13.0 Hz, 1H, CH), 4.68 (d, *J* = 13.0 Hz, 1H, CH), 3.69 (t, *J* = 5.0 Hz, 4H, $CH_2$), 3.65 (s, 3H, $CH_3$), 3.20 (t, *J* = 5.0 Hz, 4H, $CH_2$) ppm.

**$^{13}$C NMR (125 MHz, $CDCl_3$):** δ 169.7 (C=O), 151.7 (CH), 85.3 (CH), 66.0 ($CH_2$), 50.4 ($CH_3$) ppm.

**MS (EI, 70 eV):** *m*/*z* 171 [$M^+$].

***Ethyl (E)-3-morpholinoacrylate (10b)***



**10b**

Yellow viscous liquid.

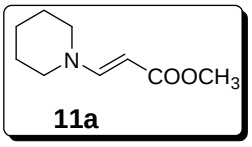
**IR (KBr) ($\nu_{max}$, cm$^{-1}$):** 1693, 1642, 1249, 988 cm$^{-1}$.

**$^1$H NMR (500 MHz, $CDCl_3$):** δ 7.36 (d, *J* = 13.0 Hz, 1H), 4.69 (d, *J* = 13.0 Hz, 1H), 4.14 (q, *J* = 7.0 Hz, 2H), 3.71 (t, *J* = 5.0 Hz, 4H), 3.21 (t, *J* = 5.0 Hz, 4H), 1.26 (t, *J* = 7.0 Hz, 3H) ppm.

**$^{13}$C NMR (125 MHz, $CDCl_3$):** δ 169.4, 151.6, 85.8, 66.0, 58.9, 14.4 ppm.

**MS (EI, 70 eV):** *m*/*z* 185 [M$^+$].

***Methyl (E)-3-(piperidin-1-yl)acrylate (11a)***



**11a**

Yellow viscous liquid.

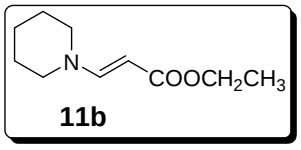
**IR (KBr):** $\nu_{max}$ 1694, 1650, 1246, 969 cm$^{-1}$.

**$^1$H NMR (500 MHz, $CDCl_3$):** δ 7.35 (d, *J* = 13.0 Hz, 1H), 4.69 (d, *J* = 13.0 Hz, 1H), 3.85 (s, 3H), 3.25-3.08 (m, 4H), 1.90-1.81 (m, 6H) ppm.

**$^{13}$C NMR (125 MHz, $CDCl_3$):** δ 169.5, 152.0, 83.6, 58.8, 50.2, 24.0 ppm.

**MS (EI, 70 eV):** *m*/*z* 169 [M$^+$].

***Ethyl (E)-3-(piperidin-1-yl)acrylate (11b)***



**11b**

Yellow viscous liquid.

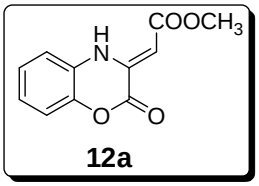
**IR (KBr):** $\nu_{max}$ 1692, 1637, 1280, 978 cm$^{-1}$.

**$^1$H NMR (500 MHz, $CDCl_3$):** δ 7.39 (d, *J* = 13.0 Hz, 1H), 4.62 (d, *J* = 13.0 Hz, 1H), 4.12 (q, *J* = 7.0 Hz, 2H), 3.20-3.19 (m, 4H), 1.65-1.56 (m, 6H), 1.25 (t, *J* = 7.0 Hz, 3H) ppm.

**$^{13}$C NMR (125 MHz, $CDCl_3$):** δ 170.0, 151.8, 83.4, 58.6, 50.7, 23.9, 14.5 ppm.

**MS (EI, 70 eV):** *m*/*z* 183 [M$^+$].

***(Z)-3-Methoxycarbonylmethylene-3,4-dihydro-2H-1,4-benzoxazin-2-one (12a)***



**12a**

Yellow solid, **m.p.:** 166–168 $^o$C (Lit. 166-167 $^o$C)[39].

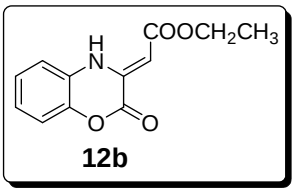
**IR (KBr):** $\nu_{max}$ 3464 (NH), 1764 (C=O), 1660 (C=O), 1628 (C=C), 1282 (C-O) cm$^{-1}$.

**$^1$H NMR (500 MHz, $CDCl_3$):** δ 10.68 (br s, 1H, NH), 7.17-7.13 (m, 2H, benzene CH), 7.05-7.02 (m, 1H, benzene CH), 6.97 (d, *J* = 8.0 Hz, 1H, benzene CH) 5.94 (s, 1H, CH), 3.78 (s, 3H, $CH_3$) ppm.

**$^{13}$C NMR (125 MHz, $CDCl_3$):** δ 170.3 (CO), 155.9 (CO), 140.0 (C), 138.1 (C), 125.7 (CH), 124.1 (C), 122.8 (CH), 117.0 (CH), 114.8 (CH), 90.7 (CH), 51.5 ($CH_3$) ppm.

**MS (EI, 70 eV):** *m*/*z* 219 [$M^+$].

***(Z)-3-Ethoxycarbonylmethylene-3,4-dihydro-2H-1,4-benzoxazin-2-one (12b)***



**12b**

Yellow solid, **m.p.:** 116–117 °C (Lit. 112 °C)[39].

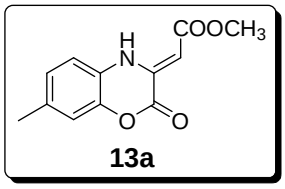
**IR (KBr):** $\nu_{max}$ 3395, 1762, 1660, 1619, 1290 $cm^{-1}$.

**$^1$H NMR (500 MHz, $CDCl_3$):** δ 10.70 (br s, 1H), 7.17-7.12 (m, 2H), 7.02 (dt, *J* = 1.5, 8.0 Hz, 1H), 6.97 (dd, *J* = 1.5, 8.0 Hz, 1H), 5.94 (s, 1H), 4.24 (q, *J* = 7.5 Hz, 2H), 1.33 (t, *J* = 7.0 Hz, 3H) ppm.

**$^{13}$C NMR (125 MHz, $CDCl_3$):** δ 170.0, 156.0, 140.0, 138.1, 125.7, 124.3, 122.7, 117.0, 114.8, 91.2, 60.4, 14.3 ppm.

**MS (EI, 70 eV):** *m*/*z* 233 [$M^+$].

***(Z)-3-Methoxycarbonylmethylene-7-methyl-3,4-dihydro-2H-1,4-benzoxazin-2-one (13a)***



**13a**

Yellow solid, **m.p.:** 170–171 °C (Lit. 168-169 °C)[37].

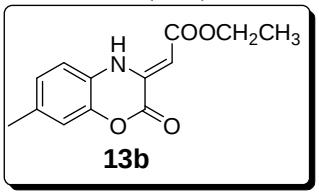
**IR (KBr):** $\nu_{max}$ 3473, 1750, 1652, 1632, 1300 $cm^{-1}$.

**$^1$H NMR (500 MHz, $CDCl_3$):** δ 10.64 (br s, 1H), 6.97-6.93 (m, 2H), 6.85 (d, *J* = 8.0 Hz, 1H), 5.89 (s, 1H), 3.77 (s, 3H), 2.32 (s, 3H) ppm.

**$^{13}$C NMR (125 MHz, $CDCl_3$):** δ 170.3, 156.1, 139.8, 138.2, 133.1, 126.3, 121.6, 117.3, 114.5, 89.9, 51.4, 20.8 ppm.

**MS (EI, 70 eV):** *m*/*z* 233 [$M^+$].

***(Z)-3-Ethoxycarbonylmethylene-7-methyl-3,4-dihydro-2H-1,4-benzoxazin-2-one (13b)***



**13b**

Yellow solid, **m.p.:** 138–139 °C.

**IR (KBr):** $\nu_{max}$ 3494, 1755, 1665, 1620, 1269 $cm^{-1}$.

**$^1$H NMR (500 MHz, $CDCl_3$):** δ 10.66 (br s, 1H), 6.98-6.93 (m, 2H),

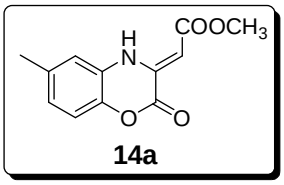
6.85 (d, *J* = 8.0 Hz, 1H), 5.90 (s, 1H), 4.23 (q, *J* = 7.0 Hz, 2H), 2.33 (s, 3H), 1.33 (t, *J* = 7.5 Hz, 3H) ppm.

**$^{13}$C NMR (125 MHz, $CDCl_3$):** δ 170.0, 156.2, 139.9, 138.1, 133.0, 126.3, 121.8, 117.3, 114.5, 90.4, 60.3, 20.8, 14.3 ppm.

**MS (EI, 70 eV):** *m*/*z* 247 [$M^+$].

***(Z)-3-Methoxycarbonylmethylene-6-methyl-3,4-dihydro-2H-1,4-benzoxazin-2-one (14a)***

Yellow solid, **m.p.:** 144 °C (Lit. 141-142 °C)[38].



**14a**

**IR (KBr):** $\nu_{max}$ 3427, 1758, 1657, 1619, 1286 $cm^{-1}$.

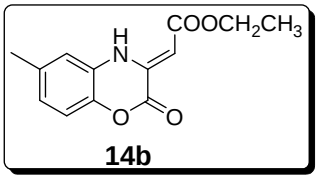
**$^1$H NMR (500 MHz, $CDCl_3$):** δ 10.61 (br s, 1H), 7.03 (d, *J* = 8.0 Hz, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 6.77 (s, 1H), 5.91 (s, 1H), 3.78 (s, 3H), 2.32 (s, 3H) ppm.

**$^{13}$C NMR (125 MHz, $CDCl_3$):** δ 170.3, 156.1, 138.2, 138.0, 135.7, 123.7, 123.5, 116.7, 115.1, 90.4, 51.4, 20.9 ppm.

**MS (EI, 70 eV):** *m*/*z* 233 [$M^+$].

***(Z)-3-Ethoxycarbonylmethylene-6-methyl-3,4-dihydro-2H-1,4-benzoxazin-2-one (14b)***

Yellow solid, **m.p.:** 105-106 °C (Lit. 98-99 °C)[36].



**14b**

**IR (KBr):** $\nu_{max}$ 3453, 1766, 1659, 1623, 1299 $cm^{-1}$.

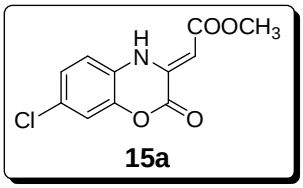
**$^1$H NMR (500 MHz, $CDCl_3$):** δ 10.64 (br s, 1H), 7.03 (d, *J* = 8.5 Hz, 1H), 6.83-6.80 (m, 1H), 6.77 (s, 1H), 5.91 (s, 1H), 4.23 (q, *J* = 7.0 Hz, 2H), 2.33 (s, 3H), 1.33 (t, *J* = 7.0 Hz, 3H) ppm.

**$^{13}$C NMR (125 MHz, $CDCl_3$):** δ 169.9, 156.1, 138.1, 138.0, 135.7, 123.8, 123.4, 116.6, 115.0, 90.9, 60.3, 20.9, 14.2 ppm.

**MS (EI, 70 eV):** *m*/*z* 247 [$M^+$].

***(Z)-3-Methoxycarbonylmethylene-7-chloro-3,4-dihydro-2H-1,4-benzoxazin-2-one (15a)***

Dark green solid, **m.p.:** 172-173 °C.



**15a**

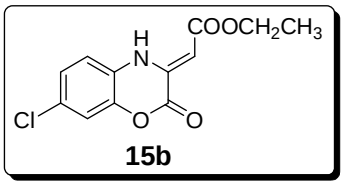
**IR (KBr):** $\nu_{max}$ 3463, 1760, 1662, 1628, 1286 $cm^{-1}$.

**$^1$H NMR (500 MHz, $CDCl_3$):** δ 10.68 (br s, 1H), 7.17 (d, *J* = 2.0 Hz, 1H), 7.12 (dd, *J* = 2.5, 8.5 Hz, 1H), 6.90 (d, *J* = 9.0 Hz, 1H), 5.96 (s, 1H), 3.79 (s, 3H) ppm.

**$^{13}$C NMR (125 MHz, $CDCl_3$):** δ 170.1, 155.2, 140.2, 137.4, 127.6, 125.8, 123.0, 117.3, 115.5, 91.6, 51.6 ppm.

**MS (EI, 70 eV):** *m*/*z* 253 [$M^+$].

***(Z)-3-Ethoxycarbonylmethylene-7-chloro-3,4-dihydro-2H-1,4-benzoxazin-2-one (15b)***



**15b**

Yellow solid, **m.p.:** 151 °C.

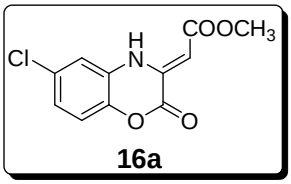
**IR (KBr):** $\nu_{max}$ 3460, 1769, 1663, 1621, 1288 $cm^{-1}$.

**$^1$H NMR (500 MHz, $CDCl_3$):** δ 10.70 (br s, 1H), 7.17 (d, 1H *J* = 2.0 Hz), 7.11 (dd, *J* = 2.0, 8.5 Hz, 1H), 6.90 (d, *J* = 8.5 Hz, 1H), 5.95 (s, 1H), 4.24 (q, *J* = 7.5 Hz, 2H), 1.33 (t, *J* = 7.0 Hz, 3H) ppm.

**$^{13}$C NMR (125 MHz, $CDCl_3$):** δ 169.8, 155.3, 140.1, 137.3, 127.4, 125.7, 123.0, 117.3, 115.5, 92.0, 60.5, 14.2 ppm.

**MS (EI, 70 eV):** *m*/*z* 267 [$M^+$].

***(Z)-3-Methoxycarbonylmethylene-6-chloro-3,4-dihydro-2H-1,4-benzoxazin-2-one (16a)***



**16a**

Yellow solid, **m.p.:** 165–166 °C (Lit. 162-164 °C)[37].

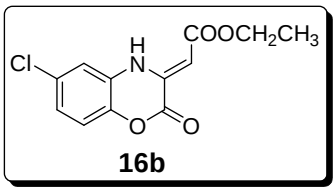
**IR (KBr):** $\nu_{max}$ 3386, 1778, 1654, 1631, 1288 $cm^{-1}$.

**$^1$H NMR (500 MHz, $CDCl_3$):** δ 10.65 (br s, 1H), 7.09-7.06 (m, 1H), 6.99-6.96 (m, 2H), 5.97 (s, 1H), 3.79 (s, 3H) ppm.

**$^{13}$C NMR (125 MHz, $CDCl_3$):** δ 170.1, 155.4, 138.6, 137.4, 130.9, 125.1, 122.6, 118.1, 114.7, 92.2, 51.7 ppm.

**MS (EI, 70 eV):** *m*/*z* 253 [$M^+$].

***(Z)-3-Ethoxycarbonylmethylene-6-chloro-3,4-dihydro-2H-1,4-benzoxazin-2-one (16b)***



**16b**

Yellow solid, **m.p.:** 123–124 °C (Lit. 122-123 °C)[36].

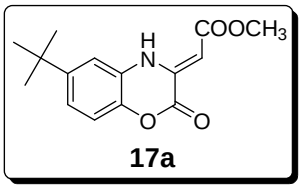
**IR (KBr):** $\nu_{max}$ 3320, 1776, 1678, 1633, 1289 $cm^{-1}$.

**$^1$H NMR (500 MHz, $CDCl_3$):** δ 10.69 (br s, 1H), 7.09-7.07 (m, 1H), 6.99-6.96 (m, 2H), 5.97 (s, 1H), 4.25 (q, *J* = 7.0 Hz, 2H), 1.33 (t, *J* = 7.0 Hz, 3H) ppm.

**$^{13}$C NMR (125 MHz, $CDCl_3$):** δ 169.7, 155.4, 138.5, 137.3, 130.8, 125.1, 122.5, 118.1, 114.6, 92.6, 60.6, 14.2 ppm.

**MS (EI, 70 eV):** *m*/*z* 267 [$M^+$].

***(Z)-3-Methoxycarbonylmethylene-6-t-butyl-3,4-dihydro-2H-1,4-benzoxazin-2-one (17a)***



**17a**

Yellow solid, **m.p.:** 84–85 $^{o}$C.

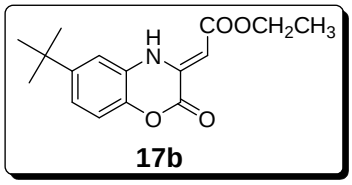
**IR (KBr):** $\nu_{max}$ 3461, 1773, 1668, 1621, 1276 cm$^{-1}$.

**$^{1}$H NMR (500 MHz, CDCl$_3$):** δ 10.70 (br s, 1H), 7.08 (d, *J* = 8.5 Hz, 1H), 7.05 (dd, *J* = 2.0, 9.0 Hz, 1H), 6.97 (d, *J* = 2.0 Hz, 1H), 5.92 (s, 1H), 3.80 (s, 3H), 1.29 (s, 9H) ppm.

**$^{13}$C NMR (125 MHz, CDCl$_3$):** δ 170.4, 156.1, 147.6, 138.4, 137.8, 123.4, 120.0, 116.4, 111.9, 90.2, 61.3, 36.0, 31.3 ppm.

**MS (EI, 70 eV):** *m*/*z* 275 [M$^{+}$].

***(Z)-3-Ethoxycarbonylmethylene-6-t-butyl-3,4-dihydro-2H-1,4-benzoxazin-2-one (17b)***



**17b**

Yellow solid, **m.p.:** 123–124 $^{o}$C.

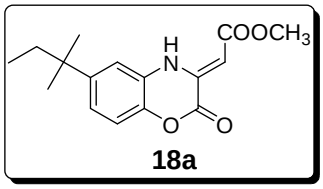
**IR (KBr):** $\nu_{max}$ 3431, 1759, 1669, 1632, 1278 cm$^{-1}$.

**$^{1}$H NMR (500 MHz, CDCl$_3$):** δ 10.72 (br s, 1H), 7.08 (d, *J* = 8.5 Hz, 1H), 7.04 (dd, *J* = 2.5, 9.0 Hz, 1H), 6.97 (d, *J* = 2.0 Hz, 1H), 5.91 (s, 1H), 4.25 (q, *J* = 7.0 Hz, 2H), 1.34 (t, *J* = 7.5 Hz, 3H), 1.30 (s, 9H) ppm.

**$^{13}$C NMR (125 MHz, CDCl$_3$):** δ 170.1, 156.2, 149.3, 138.3, 137.9, 123.5, 119.9, 116.4, 111.9, 90.7, 60.3, 34.6, 31.3, 14.3 ppm.

**MS (EI, 70 eV):** *m*/*z* 289 [M$^{+}$].

***(Z)-3-Methoxycarbonylmethylene-6-t-pentyl-3,4-dihydro-2H-1,4-benzoxazin-2-one (18a)***



**18a**

Yellow solid, **m.p.:** 57–58 $^{o}$C.

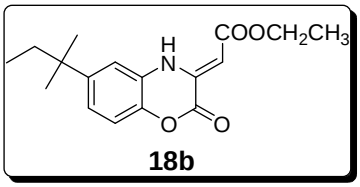
**IR (KBr):** $\nu_{max}$ 3430, 1779, 1658, 1625, 1281 cm$^{-1}$.

**$^{1}$H NMR (500 MHz, CDCl$_3$):** δ 10.70 (br s, 1H), 7.08 (d, *J* = 8.5 Hz, 1H), 6.98 (dd, *J* = 2.0, 8.5 Hz, 1H), 6.91 (d, *J* = 2.0 Hz, 1H), 5.93 (s, 1H), 3.78 (s, 3H), 1.62 (q, *J* = 7.5 Hz, 2H), 1.27 (s, 6H), 0.67 (t, *J* = 7.5 Hz, 3H) ppm.

**$^{13}$C NMR (125 MHz, CDCl$_3$):** δ 170.1, 156.2, 147.6, 138.3, 137.8, 123.5, 120.6, 116.4, 112.6, 90.6, 60.3, 37.9, 36.8, 28.4, 9.0 ppm.

**MS (EI, 70 eV):** *m*/*z* 289 [M$^{+}$].

***(Z)-3-Ethoxycarbonylmethylene-6-t-pentyl-3,4-dihydro-2H-1,4-benzoxazin-2-one (18b)***



**18b**

Yellow solid, **m.p.:** 69–70 $^{o}$C.

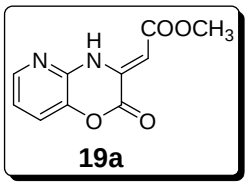
**IR (KBr):** $\nu_{max}$ 3500, 1763, 1659, 1630, 1283 cm$^{-1}$.

**$^{1}$H NMR (500 MHz, CDCl$_3$):** δ 10.72 (br s, 1H), 7.08 (d, *J* = 8.5 Hz, 1H), 6.97 (dd, *J* = 2.0, 8.5 Hz, 1H), 6.91 (d, *J* = 2.0 Hz, 1H), 5.91 (s, 1H), 4.24 (q, *J* = 7.0 Hz, 2H), 1.62 (q, *J* = 7.5 Hz, 2H), 1.33 (t, *J* = 7.5 Hz, 3H), 1.26 (s, 6H), 0.67 (t, *J* = 7.5 Hz, 3H) ppm.

**$^{13}$C NMR (125 MHz, CDCl$_3$):** δ 170.0, 156.2, 147.6, 138.3, 137.8, 123.5, 120.5, 116.3, 112.5, 90.5, 60.3, 37.8, 36.7, 28.4, 14.2, 9.0 ppm.

**MS (EI, 70 eV):** *m*/*z* 303 [M$^{+}$].

***(Z)-3-Methoxycarbonylmethylene-3,4-dihydro-2H-5-aza-1,4-benzoxazin-2-one (19a)***



**19a**

Brown solid, **m.p.:** >235 $^{o}$C (decomp.)

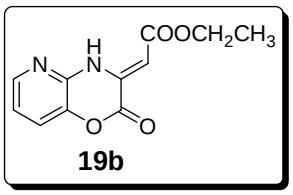
**IR (KBr):** $\nu_{max}$ 3439, 1734, 1676, 1607, 1283 cm$^{-1}$.

**$^{1}$H NMR (500 MHz, DMSO-*d*$_6$):** δ 12.11 (br s, 1H), 8.07 (d, *J* = 4.5 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.15-7.12 (m, 1H), 6.06 (s, 1H), 3.71 (s, 3H) ppm.

**$^{13}$C NMR (125 MHz, CDCl$_3$ & DMSO-*d*$_6$):** δ 161.8, 153.6, 148.9, 141.0, 137.2, 134.4, 121.0, 117.5, 97.3, 49.4 ppm.

**MS (EI, 70 eV):** *m*/*z* 220 [M$^{+}$].

***(Z)-3-Ethoxycarbonylmethylene-3,4-dihydro-2H-5-aza-1,4-benzoxazin-2-one (19b)***



**19b**

Brown solid, **m.p.:** >211–213 $^{o}$C (decomp.)

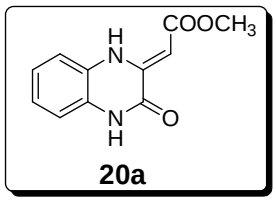
**IR (KBr):** $\nu_{max}$ 3452, 1705, 1663, 1613, 1277 cm$^{-1}$.

**$^{1}$H NMR (500 MHz, CDCl$_3$):** δ 11.19 (br br s, 1H), 8.20 (d, *J* = 5.0 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.13-7.09 (m, 1H), 6.42 (s, 1H), 4.27 (q, *J* = 7.0 Hz, 2H), 1.34 (t, *J* = 7.0 Hz, 3H) ppm.

**$^{13}$C NMR (125 MHz, CDCl$_3$):** δ 163.9, 155.8, 149.7, 142.4, 139.0, 136.8, 124.2, 119.8, 102.6, 60.6, 14.2 ppm.

**MS (EI, 70 eV):** *m*/*z* 234 [M$^{+}$].

***(Z)-3-Methoxycarbonylmethylene-3,4-dihydro-2(1H) quinoxalinone (20a)***



**20a**

Brown solid, **m.p.:** >227 °C (decomp.) (Lit. >225 °C, decomp.)[35].

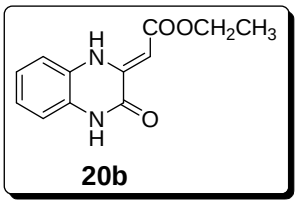
**IR (KBr):** $\nu_{max}$ 3425 (NH), 3260 (NH), 1689 (C=O), 1649 (C=O), 1613 (C=C), 1269 (C-O) $cm^{-1}$.

**$^1$H NMR (500 MHz, DMSO-*d*$_6$):** δ 11.74 (br s, 1H, NH), 11.03 (br s, 1H, NH), 7.40 (d, *J* = 7.5 Hz, 1H, benzene CH), 7.08-6.90 (m, 3H, benzene CH), 5.52 (s, 1H, CH), 3.68 (s, 3H, $CH_3$) ppm.

**$^{13}$C NMR (125 MHz, DMSO-*d*$_6$):** δ 169.5 (CO), 155.6 (CO), 144.0 (C), 125.1 (C), 124.8 (C), 123.5 (CH), 122.5 (CH), 115.4 (CH), 115.2 (CH), 83.4 (CH), 50.7 ($CH_3$) ppm.

**MS (EI, 70 eV):** *m*/*z* 218 [$M^+$].

***(Z)-3-Ethoxycarbonylmethylene-3,4-dihydro-2(1H) quinoxalinone (20b)***



**20b**

Yellow solid**, m.p.:** >216–217 °C (decomp.) (Lit. 218 °C)[33].

**IR (KBr):** $\nu_{max}$ 3386, 3256, 1684, 1647, 1622, 1273 $cm^{-1}$.

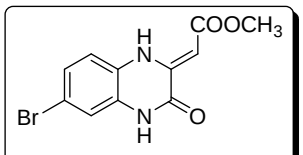
**$^1$H NMR (500 MHz, DMSO-*d*$_6$):** δ 11.74 (br s, 1H), 11.06 (br s, 1H), 7.40 (dd, *J* = 1.5, 8.0 Hz, 1H), 7.08-6.99 (m, 3H), 5.49 (s, 1H), 4.15 (q, *J* = 7.5 Hz, 2H), 1.24 (t, *J* = 7.0 Hz, 3H) ppm.

**$^{13}$C NMR (125 MHz, DMSO-*d*$_6$):** δ 169.2, 155.6, 144.0, 125.1, 124.8, 123.4, 122.5, 115.4, 115.3, 83.7, 59.1, 14.3 ppm.

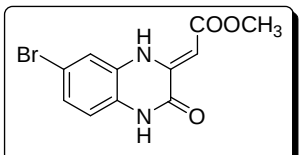
**MS (EI, 70 eV):** *m*/*z* 232 [$M^+$].

***(Z)-3-Methoxycarbonylmethylene-7-bromo-3,4-dihydro-2(1H) quinoxalinone (21a - Major)***

***(Z)-3-Methoxycarbonylmethylene-6-bromo-3,4-dihydro-2(1H) quinoxalinone (21a - Minor)***



**21a (major)**



**21a (minor)**

Brown solid, **m.p.:** >235–236 °C (decomp.)

**IR (KBr):** $\nu_{max}$ 3398, 3215, 1693, 1667, 1613, 1273 $cm^{-1}$.

**$^1$H NMR (500 MHz, DMSO-*d*$_6$):** δ 11.78 (br s, 1H, minor), 11.77 (br s, 1H, major), 10.99 (br s, 1H, major), 10.95 (br s, 1H, minor), 7.75 (d, *J* = 1.5 Hz, 1H, minor), 7.40 (d, *J* = 8.5 Hz, 1H, major), 7.20-7.13 (m, 2H major and 1H minor), 6.96 (d, *J* = 8.5 Hz, 1H, minor), 5.54 (s, 1H, minor), 5.53 (s, 1H, major), 3.68 (s, 3H, major), 3.68 (s, 3H, minor) ppm.

**$^{13}$C NMR (125 MHz, DMSO-$d_6$, Major):** δ 169.4, 155.5, 143.3, 126.7, 125.8, 124.5, 117.9, 117.3, 113.5, 84.4, 50.8 ppm.

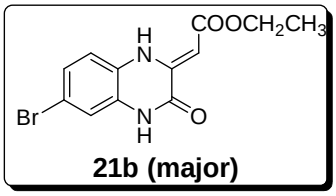
**$^{13}$C NMR (125 MHz, DMSO-$d_6$, Minor):** δ 169.0, 155.4, 143.2, 126.4, 124.8, 124.4, 117.7, 116.8, 114.9, 84.9, 51.9 ppm.

**MS (EI, 70 eV):** *m*/*z* 296 [$M^+$].

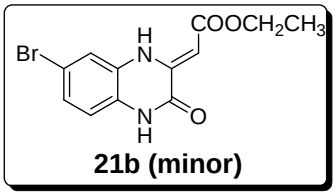
***(Z)-3-Ethoxycarbonylmethylene-7-bromo-3,4-dihydro-2(1H) quinoxalinone (21b - Major)***
***(Z)-3-Ethoxycarbonylmethylene-6-bromo-3,4-dihydro-2(1H) quinoxalinone (21b - Minor)***

Dark brown solid, **m.p.:** >215 °C (decomp.)

**IR (KBr):** $\nu_{max}$ 3373, 3216, 1692, 1656, 1621, 1268 cm$^{-1}$**.**



**21b (major)**



**21b (minor)**

**$^{1}$H NMR (500 MHz, DMSO-$d_6$):** δ 11.78 (br s, 1H, minor), 11.77 (br s, 1H, major), 11.03 (br s, 1H, major), 10.99 (br s, 1H, minor), 7.75 (d, *J* = 1.0 Hz, 1H, minor), 7.41 (d, *J* = 8.5 Hz, 1H, major), 7.20-7.13 (m, 2H major and 1H minor), 6.96 (d, *J* = 8.5 Hz, 1H, minor), 5.52 (s, 1H, minor), 5.51 (s, 1H, major), 4.16 (q, *J* = 7.0 Hz, 2H, minor), 4.13 (q, *J* = 7.0 Hz, 2H, major), 1.24 (t, *J* = 6.5 Hz, 3H major and 3H minor) ppm.

**$^{13}$C NMR (125 MHz, DMSO-$d_6$, Major):** δ168.9, 155.5, 143.3, 126.7, 125.8, 124.6, 117.3, 117.3, 113.5, 84.7, 59.3, 14.3 ppm.

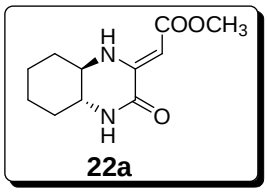
**$^{13}$C NMR (125 MHz, DMSO-$d_6$, Minor):** *δ* 168.7, 155.5, 143.2, 126.5, 124.8, 124.4, 117.9, 116.8, 114.9, 85.2, 59.3, 14.3 ppm.

**MS (EI, 70 eV):** *m*/*z* 310 [$M^+$].

***(Z)-3-Methoxycarbonylmethylene-octahydro-3,4-dihydro-2(1H) quinoxalinone (22a)***

Brown solid, **m.p.:** 174-175 °C (Lit. 162 °C)[33].

**IR (KBr):** $\nu_{max}$ 3447, 3295, 1692, 1661, 1619, 1279 cm$^{-1}$.



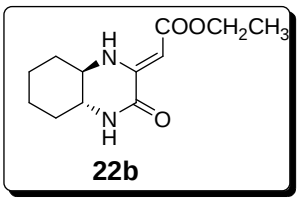
**22a**

**$^{1}$H NMR (500 MHz, DMSO-$d_6$):** *δ* 8.55 (br s, 1H), 8.05 (br s, 1H), 5.27 (s, 1H), 3.58 (s, 3H), 3.18-3.11 (m, 1H), 3.07-3.01 (m, 1H), 1.96 (d, *J* = 10.5 Hz, 1H), 1.86 (d, *J* = 10.0 Hz, 1H), 1.68 (t, *J* = 10.0 Hz, 2H), 1.34-1.16 (m, 4H) ppm.

**$^{13}$C NMR (125 MHz, DMSO-$d_6$):** *δ* 169.8, 159.7, 150.2, 83.6, 54.6, 54.4, 50.4, 29.0, 23.4, 23.1 ppm.

**MS (EI, 70 eV):** *m*/*z* 224 [$M^+$].

***(Z)-3-Ethoxycarbonylmethylene-octahydro-3,4-dihydro-2(1H) quinoxalinone (22b)***



**22b**

Brown solid, **m.p.:** 143 °C (Lit. 194-195 °C)[40].

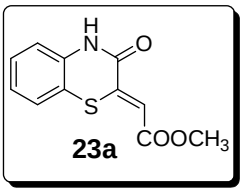
**IR (KBr):** $\nu_{max}$ 3457, 3288, 1686, 1649, 1611, 1268 $cm^{-1}$.

**$^1$H NMR (500 MHz, DMSO-$d_6$):** $\delta$ 8.53 (br s, 1H), 8.05 (br s, 1H), 5.25 (s, 1H), 4.05 (q, $J$ = 7.0 Hz, 2H), 3.17-3.11 (m, 1H), 3.07-3.00 (m, 1H), 1.95 (d, $J$ = 10.0 Hz, 1H), 1.87 (d, $J$ = 10.5 Hz, 1H), 1.68 (t, $J$ = 10.0 Hz, 2H), 1.34-1.20 (m, 4H), 1.18 (t, $J$ = 7.0 Hz, 3H) ppm.

**$^{13}$C NMR (125 MHz, DMSO-$d_6$):** $\delta$ 169.6, 159.9, 150.2, 84.1, 58.8, 54.7, 54.5, 29.1, 23.5, 23.2, 14.5 ppm.

**MS (EI, 70 eV):** $m/z$ 238 [$M^+$].

***2-Methoxycarbonylmethylene-3,4-dihydro-2H-1,4-benzthiazin-3-one (23a)***



**23a**

Yellow solid, **m.p.:** >235 °C (decomp.) (Lit. >235-237 °C, decomp.)[34].

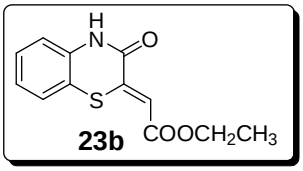
**IR (KBr):** $\nu_{max}$ 3179 (NH), 1663 (C=O), 1590 (C=O), 1557 (C=C), 1199 (C-O) $cm^{-1}$.

**$^1$H NMR (500 MHz, DMSO-$d_6$):** $\delta$ 11.55 (br s, 1H, NH), 7.42 (dd, $J$ = 0.5, 8.0 Hz, 1H, benzene CH), 7.25 (dt, $J$ = 1.0, 8.0 Hz, 1H, benzene CH), 7.13 (dd, $J$ = 1.0, 8.0 Hz, 1H, benzene CH), 7.09 (t, $J$ = 7.5 Hz, 1H, benzene CH) 6.92 (s, 1H, CH), 3.73 (s, 3H, $CH_3$) ppm.

**$^{13}$C NMR (125 MHz, DMSO-$d_6$):** $\delta$ 165.9 (CO), 154.2 (CO), 141.0 (C), 132.7 (C), 127.2 (CH), 125.2 (CH), 123.4 (CH), 117.1 (CH), 115.0 (C), 113.7 (CH), 51.7 ($CH_3$) ppm.

**MS (EI, 70 eV):** $m/z$ 235 [$M^+$].

***2-Ethoxycarbonylmethylene-3,4-dihydro-2H-1,4-benzthiazin-3-one (23b)***



**23b**

Yellow solid, **m.p.:** >216–217 °C (decomp.) (Lit. 208-211 °C, decomp.)[34].

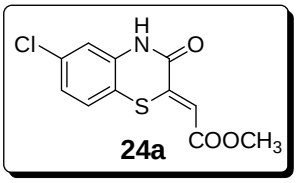
**IR (KBr):** $\nu_{max}$ 3267, 1670, 1593, 1560, 1199 $cm^{-1}$.

**$^1$H NMR (500 MHz, DMSO-$d_6$):** $\delta$ 11.54 (br s, 1H), 7.43 (d, $J$ = 7.5 Hz, 1H), 7.26 (dt, $J$ = 1.0, 8.5 Hz, 1H), 7.14 (d, $J$ = 8.0 Hz, 1H), 7.10 (dt, $J$ = 1.0, 8.0 Hz, 1H), 6.91 (s, 1H), 4.20 (q, $J$ = 7.0 Hz, 2H), 1.26 (t, $J$ = 7.0 Hz, 3H) ppm.

**$^{13}$C NMR (125 MHz, DMSO-$d_6$):** $\delta$ 165.4, 154.2, 140.9, 132.7, 127.2, 125.2, 123.4, 117.0, 115.0, 114.0, 60.4, 14.1 ppm.

**MS (EI, 70 eV):** *m*/*z* 249 [$M^+$].

***2-Methoxycarbonylmethylene-6-chloro-3,4-dihydro-2H-1,4-benzthiazin-3-one (24a)***




Yellow solid, **m.p.:** >251–252 $^oC$ (decomp.)

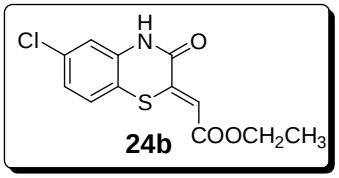
**IR (KBr):** $\nu_{max}$ 3173, 1667, 1580, 1558, 1190 $cm^{-1}$.

**$^1$H NMR (500 MHz, DMSO-*d*$_6$):** $\delta$ 11.61 (br s, 1H), 7.46 (d, *J* = 8.5 Hz, 1H), 7.17-7.12 (m, 2H), 6.89 (s, 1H), 3.72 (s, 3H) ppm.

**$^{13}$C NMR (125 MHz, DMSO-*d*$_6$):** $\delta$ 165.4, 154.1, 140.0, 134.0, 131.1, 126.9, 123.0, 116.2, 114.5, 114.2, 60.5 ppm.

**MS (EI, 70 eV):** *m*/*z* 269 [$M^+$].

***2-Ethoxycarbonylmethylene-6-chloro-3,4-dihydro-2H-1,4-benzthiazin-3-one (24b)***




Yellow solid, **m.p.:** >236 $^oC$ (Lit. 236 $^oC$)[23] (decomp.)

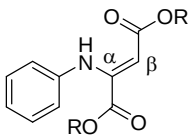
**IR (KBr):** $\nu_{max}$ 3175, 1669, 1587, 1563, 1192 $cm^{-1}$.

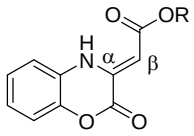
**$^1$H NMR (500 MHz, DMSO-*d*$_6$):** $\delta$ 11.63 (br s, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.18-7.13 (m, 2H), 6.90 (s, 1H), 4.20 (q, *J* = 7.0 Hz, 2H), 1.26 (t, *J* = 7.0 Hz, 3H) ppm.

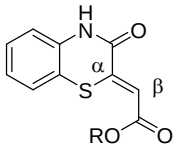
**$^{13}$C NMR (125 MHz, DMSO-*d*$_6$):** $\delta$ 165.3, 154.1, 140.5, 134.0, 131.2, 126.8, 123.1, 116.2, 114.4, 113.9, 60.5, 14.1 ppm.

**MS (EI, 70 eV):** *m*/*z* 283 [$M^+$].

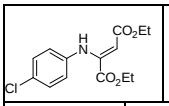
**Table:** Selected data of absorption frequencies of vinylic C=C and carbonyl bonds and $^{1}H$ and $^{13}C$ NMR chemical shifts.[a]




| Adduct | IR (ν in $cm^{-1}$) | | | $^{1}H$ (δ in ppm) Vinylic CH | $^{13}C$ (δ in ppm) | | |
|---|---|---|---|---|---|---|---|
| | α C=O | β C=O | Vinylic C=C | | Vinylic CH | Ring C=O | Ester C=O |
| **1a** | 1739 | 1672 | 1605 | 5.39 | 93.5 | 164.7 | 169.5 |
| **1b** | 1738 | 1667 | 1597 | 5.40 | 93.8 | 164.4 | 169.6 |
| **2a** | 1739 | 1669 | 1611 | 5.30 | 91.6 | 164.8 | 170.0 |
| **2b** | 1737 | 1665 | 1612 | 5.29 | 91.9 | 164.4 | 169.8 |
| **3a** | 1739 | 1672 | 1617 | 5.45 | 94.8 | 164.4 | 169.7 |
| **3b** | 1736 | 1668 | 1616 | 5.44 | 95.0 | 164.0 | 169.4 |
| **4a** | 1741 | 1671 | 1599 | 5.33 | 92.8 | 165.0 | 169.8 |
| **4b** | 1737 | 1667 | 1599 | 5.33 | 93.1 | 164.6 | 169.6 |
| **5a** | 1742 | 1675 | 1609 | 5.33 | 92.5 | 164.9 | 170.0 |
| **5b** | 1737 | 1667 | 1610 | 5.33 | 92.7 | 164.4 | 169.7 |
| **6a** | 1741 | 1681 | 1601 | 5.36 | 93.2 | 165.0 | 169.9 |
| **6b** | 1735 | 1668 | 1609 | 5.35 | 93.4 | 164.5 | 169.6 |
| **7a** | 1745 | 1677 | 1591 | 5.20 | 88.0 | 164.1 | 170.5 |
| **7b** | 1734 | 1662 | 1606 | 5.18 | 88.2 | 163.7 | 170.2 |
| **8a** | 1742 | 1695 | 1584 | 4.80 | 87.0 | 165.7 | 167.7 |
| **8b** | 1739 | 1693 | 1584 | 4.81 | 87.6 | 165.4 | 167.2 |
| **9a** | 1740 | 1664 | 1609 | 5.05 | 84.2 | 164.3 | 172.0 |
| **9b** | 1734 | 1662 | 1606 | 5.03 | 88.2 | 163.7 | 170.2 |
| **10a** | | 1699 | 1641 | 4.68 & 7.35 | 85.3 | 151.7 | 169.7 |
| **10b** | | 1693 | 1642 | 4.69 & 7.36 | 85.8 | 151.6 | 169.4 |
| **11a** | | 1694 | 1650 | 4.69 & 7.35 | 83.6 | 152.0 | 169.5 |
| **11b** | | 1684 | 1637 | 4.62 & 7.39 | 83.4 | 151.8 | 170.0 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
|  | 1736 | 1670 | 1616 | 5.44 (*Z*, major)<br>5.31 (*E*, minor) | 94.9 | 164.1 | 169.5 |
| **12a** | 1764 | 1660 | 1628 | 5.94 | 90.7 | 155.9 | 170.3 |
| **12b** | 1762 | 1660 | 1619 | 5.94 | 91.2 | 156.0 | 170.0 |
| **13a** | 1750 | 1652 | 1632 | 5.89 | 89.9 | 156.1 | 170.3 |
| **13b** | 1755 | 1665 | 1620 | 5.90 | 90.4 | 156.2 | 170.0 |
| **14a** | 1758 | 1657 | 1619 | 5.91 | 90.4 | 156.1 | 170.3 |
| **14b** | 1766 | 1659 | 1623 | 5.91 | 90.9 | 156.1 | 169.9 |
| **15a** | 1760 | 1662 | 1628 | 5.96 | 91.6 | 155.2 | 170.1 |
| **15b** | 1769 | 1663 | 1621 | 5.95 | 92.0 | 155.3 | 169.8 |
| **16a** | 1778 | 1654 | 1631 | 5.97 | 92.2 | 155.4 | 170.1 |
| **16b** | 1776 | 1678 | 1633 | 5.97 | 92.6 | 155.4 | 169.7 |
| **17a** | 1773 | 1668 | 1621 | 5.92 | 90.2 | 156.1 | 170.4 |
| **17b** | 1759 | 1669 | 1632 | 5.91 | 90.7 | 156.2 | 170.1 |
| **18a** | 1779 | 1658 | 1625 | 5.93 | 90.6 | 156.2 | 170.1 |
| **18b** | 1763 | 1659 | 1630 | 5.91 | 90.5 | 156.2 | 170.0 |
| **19a** | 1734 | 1676 | 1607 | 6.06 | 97.3 | 153.6 | 161.8 |
| **19b** | 1705 | 1663 | 1613 | 6.42 | 102.6 | 155.8 | 163.9 |
| **20a** | 1689 | 1649 | 1613 | 5.52 | 183.4 | 155.6 | 169.5 |
| **20b** | 1684 | 1647 | 1622 | 5.49 | 83.7 | 155.6 | 169.2 |
| **21a** | 1693 | 1667 | 1613 | 5.54 (minor)<br>5.53 (major) | 84.9 (minor)<br>84.4 (major) | 155.4 (minor)<br>155.5 (major) | 169.0 (minor)<br>169.4 (major) |
| **21b** | 1692 | 1656 | 1621 | 5.52 (minor)<br>5.51 (major) | 85.2 (minor)<br>84.7 (major) | 155.5 (minor)<br>155.5 (major) | 168.7 (minor)<br>168.9 (major) |
| **22a** | 1692 | 1661 | 1619 | 5.27 | 83.6 | 159.7 | 169.8 |
| **22b** | 1686 | 1649 | 1611 | 5.25 | 84.1 | 159.9 | 169.6 |
| **23a** | 1663 | 1590 | 1557 | 6.92 | 113.7 | 154.2 | 165.9 |
| **23b** | 1670 | 1593 | 1560 | 6.91 | 114.0 | 154.2 | 165.4 |
| **24a** | 1667 | 1580 | 1558 | 6.89 | 114.2 | 154.1 | 165.4 |
| **24b** | 1669 | 1587 | 1563 | 6.90 | 113.9 | 154.1 | 165.3 |

[a] NMR spectra of compounds **1a,b – 18a,b** and **19b** were recorded in $CDCl_3$ and those of compounds **20a,b – 24a,b** were recorded in DMSO-$d_6$. The $^1$H NMR spectrum of **19a** was recorded in DMSO-$d_6$ and its $^{13}$C NMR was recorded in $CDCl_3$ and DMSO-$d_6$.