

## Design, synthesis, crystal structure and fungicidal activity of (E)-5-(methoxyimino)-3,5-dihydrobenzo[e][1,2]oxazepin-4(1H)-one analogues

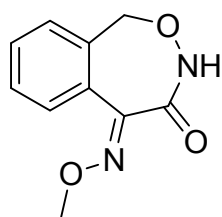
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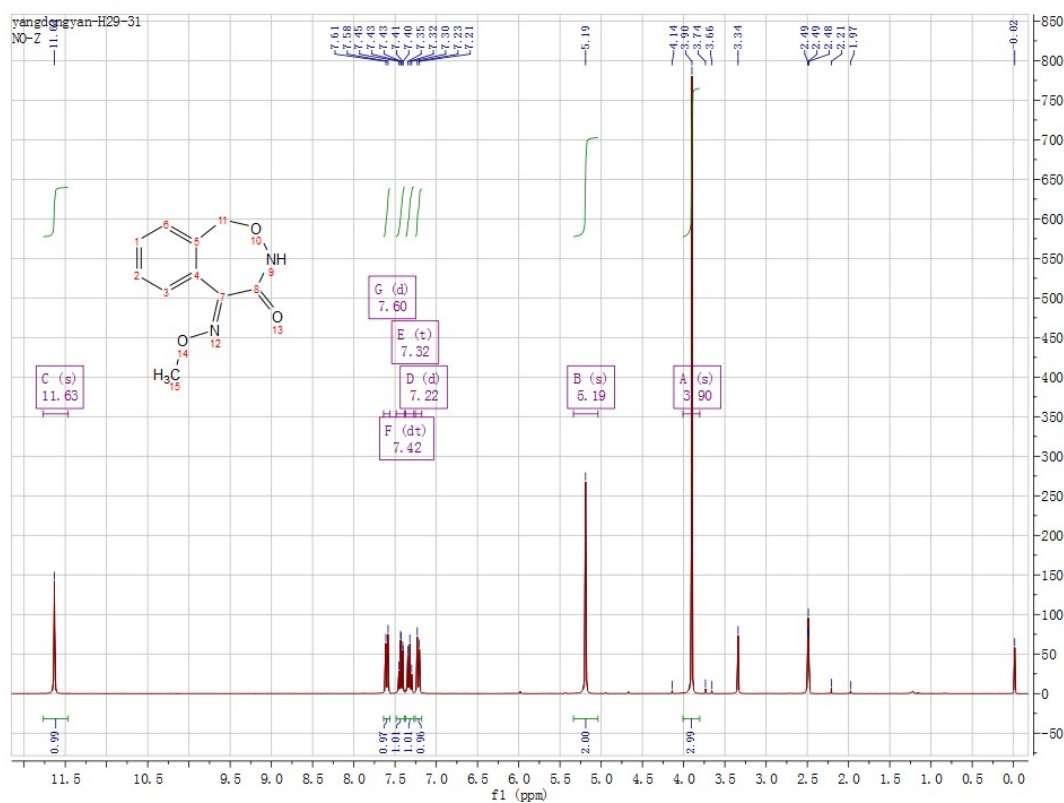
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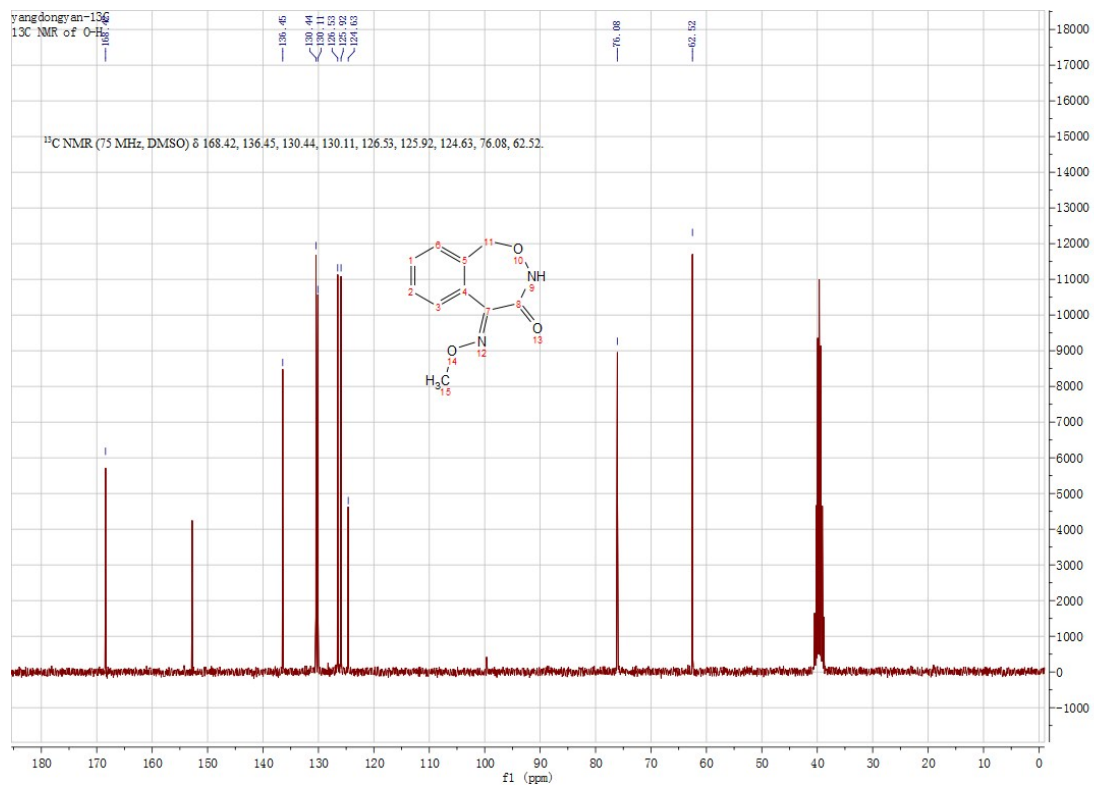
## <sup>1</sup>H NMR, <sup>13</sup>C NMR and HRMS spectrum of title compounds



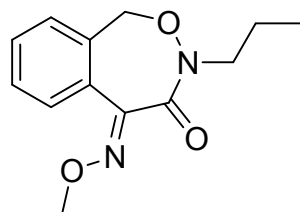
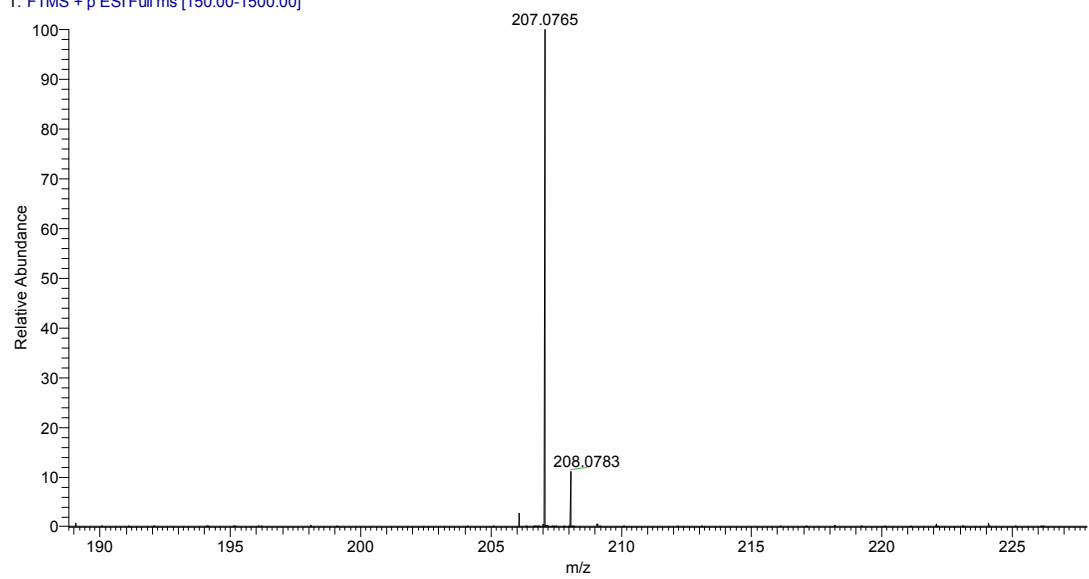
Data for (E)-5-(methoxyimino)-3,5-dihydrobenzo[e][1,2]oxazepin-4(1H)-one (**4**): yield 81 %; white solid; mp 146 °C; <sup>1</sup>H NMR (300 MHz, DMSO) δ 11.63 (s, 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.42 (dt, *J* = 7.6, 3.8 Hz, 1H), 7.32 (t, *J* = 7.1 Hz, 1H), 7.22 (d, *J* = 7.7 Hz, 1H), 5.19 (s, 2H), 3.90 (s, 3H). <sup>13</sup>C NMR (75 MHz, DMSO) δ 168.42, 136.45, 130.44, 130.11, 126.53, 125.92, 124.63, 76.08, 62.52. HRMS (ESI) *m/z* calcd for C<sub>10</sub>H<sub>10</sub>N<sub>2</sub>O<sub>3</sub> (M+H)<sup>+</sup> 207.0764, found 207.0765.

<sup>1</sup>H NMR (300 MHz, DMSO) δ 11.63 (s, 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.42 (dt, *J* = 7.6, 3.8 Hz, 1H), 7.32 (t, *J* = 7.1 Hz, 1H), 7.22 (d, *J* = 7.7 Hz, 1H), 5.19 (s, 2H), 3.90 (s, 3H).

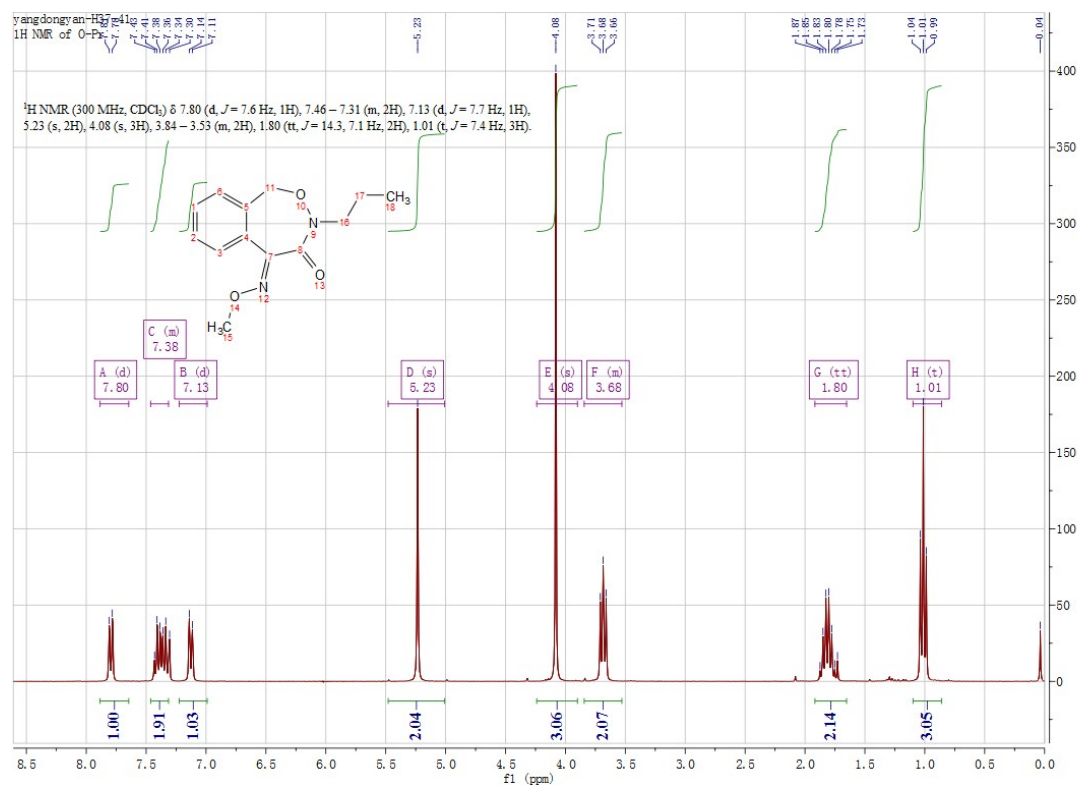


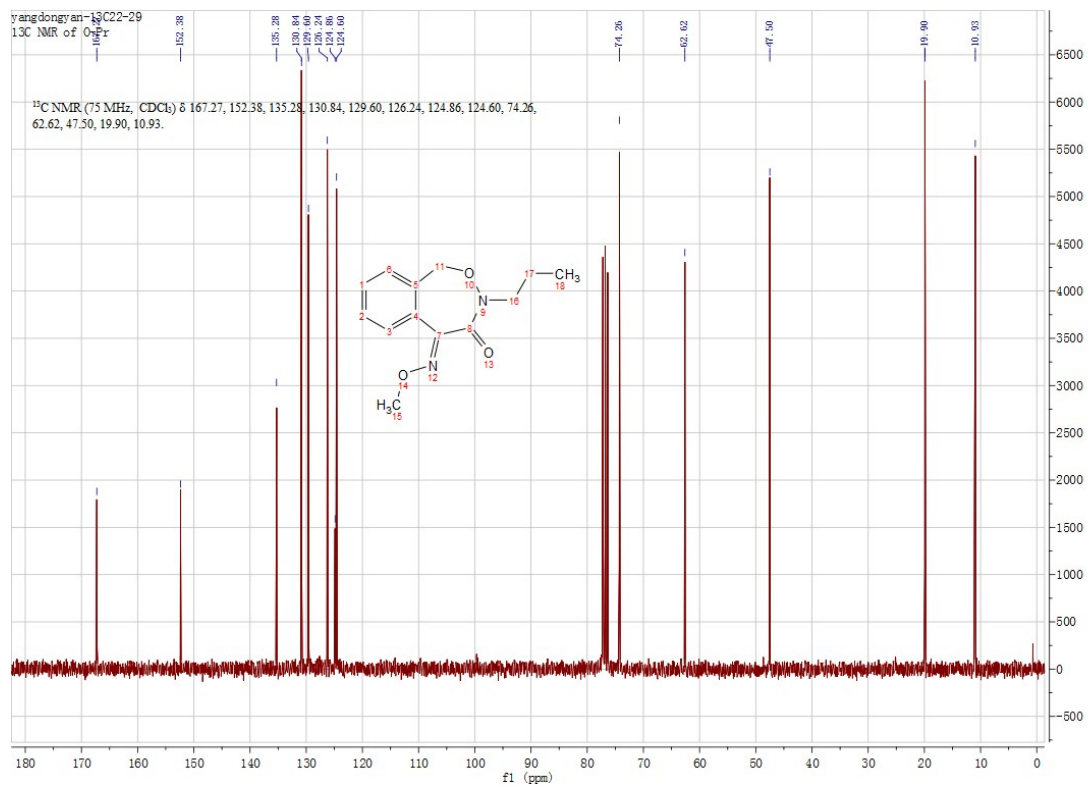


1\_160522113656 #62 RT: 0.66 AV: 1 NL: 9.02E8  
 T: FTMS + p ESI Full ms [150.00-1500.00]

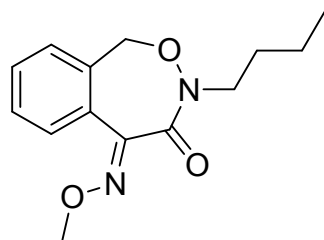
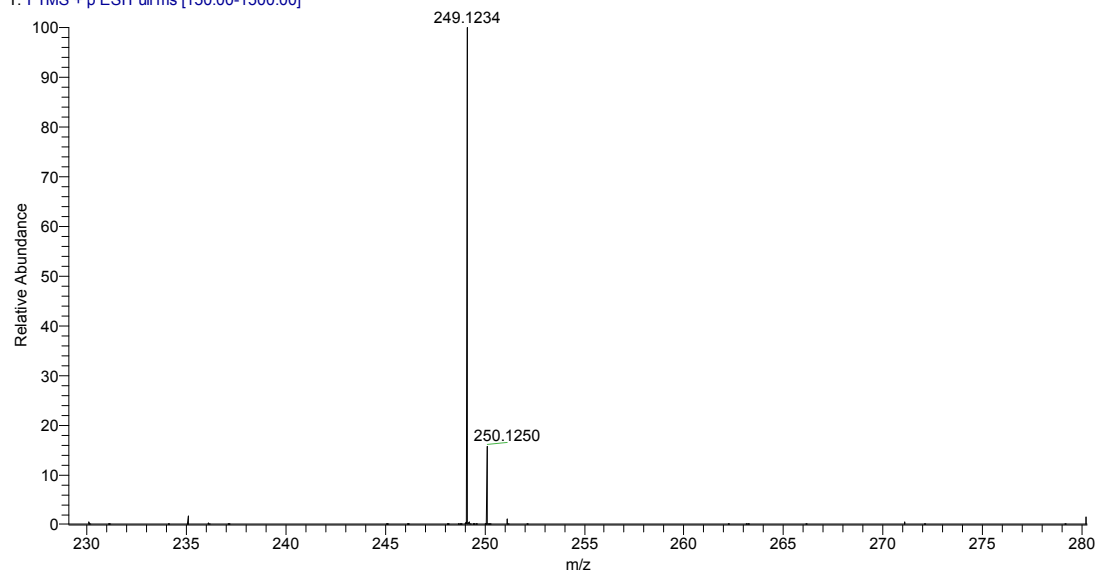


Data for (E)-5-(methoxyimino)-3-propyl-3,5-dihydrobenzo[e][1,2]oxazepin-4(1H)-one (**5-01**). White crystal; yield, 52%; mp: 83-85°C.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.80 (d,  $J = 7.6$  Hz, 1H), 7.46 – 7.31 (m, 2H), 7.13 (d,  $J = 7.7$  Hz, 1H), 5.23 (s, 2H), 4.08 (s, 3H), 3.84 – 3.53 (m, 2H), 1.80 (tt,  $J = 14.3, 7.1$  Hz, 2H), 1.01 (t,  $J = 7.4$  Hz, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  167.27, 152.38, 135.28, 130.84, 129.60, 126.24, 124.86, 124.60, 74.26, 62.62, 47.50, 19.90, 10.93. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{13}\text{H}_{16}\text{N}_2\text{O}_3$  ( $\text{M}+\text{H}$ ) $^+$  249.1234, found 249.1234.

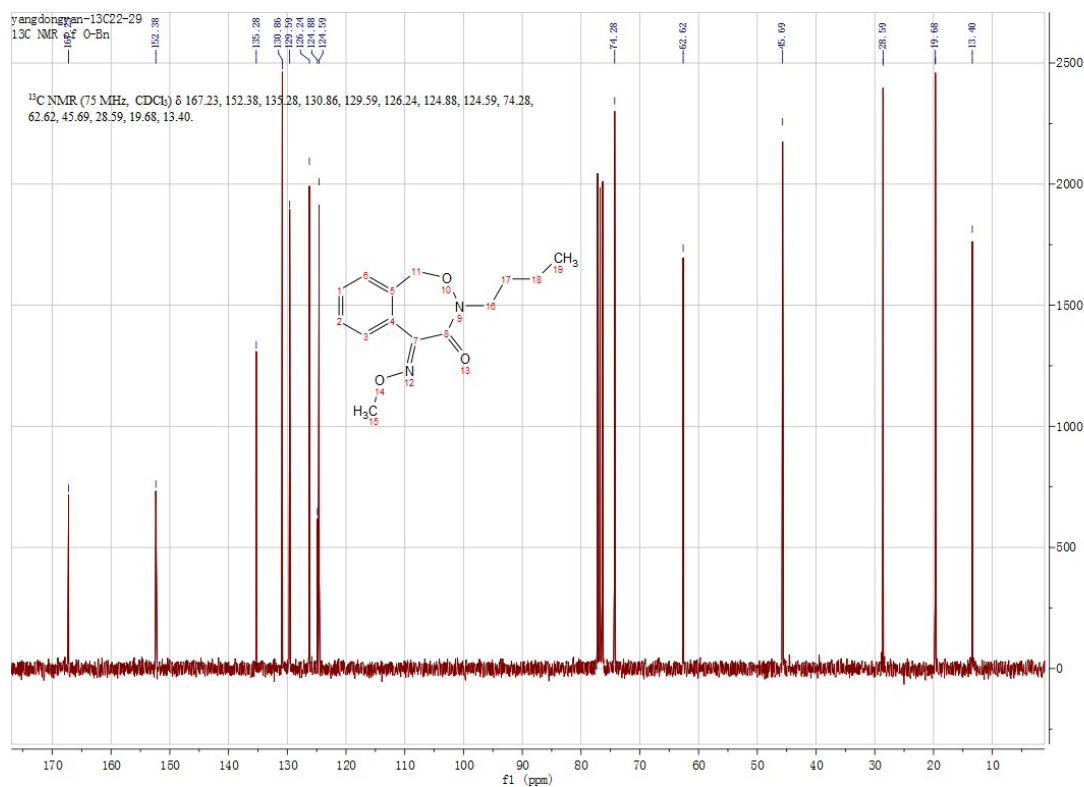
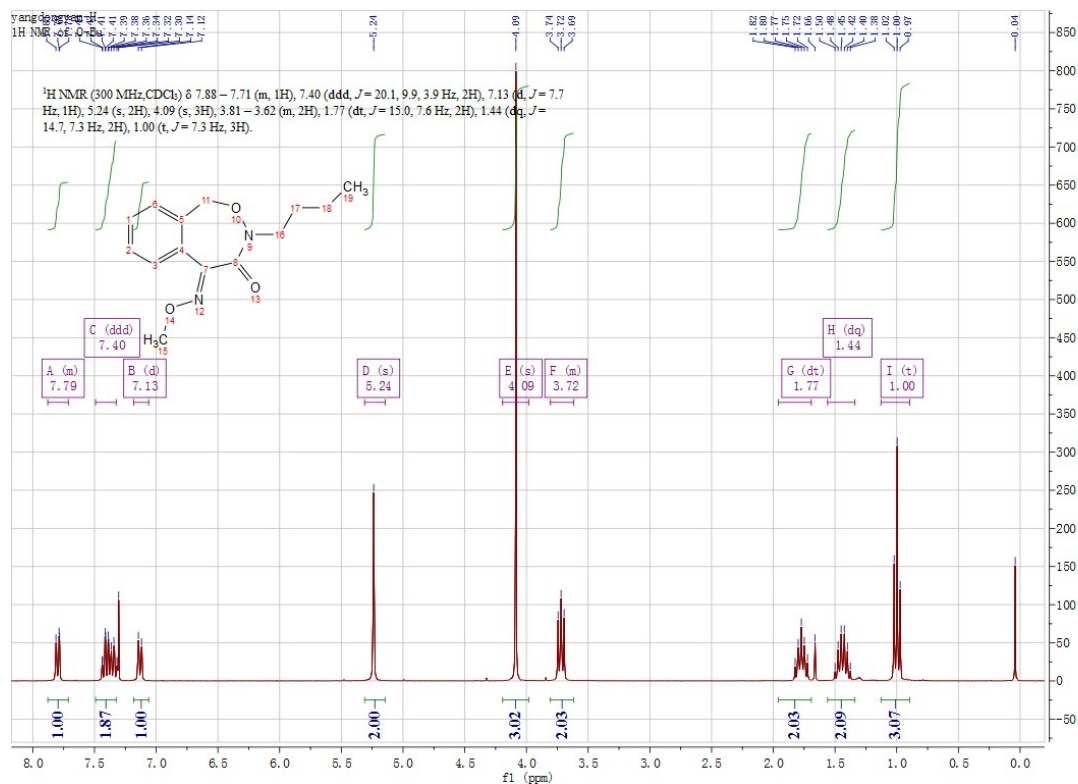




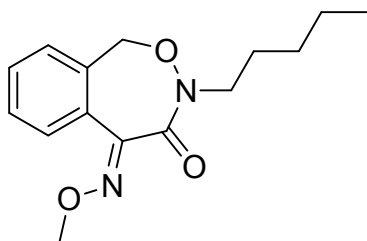
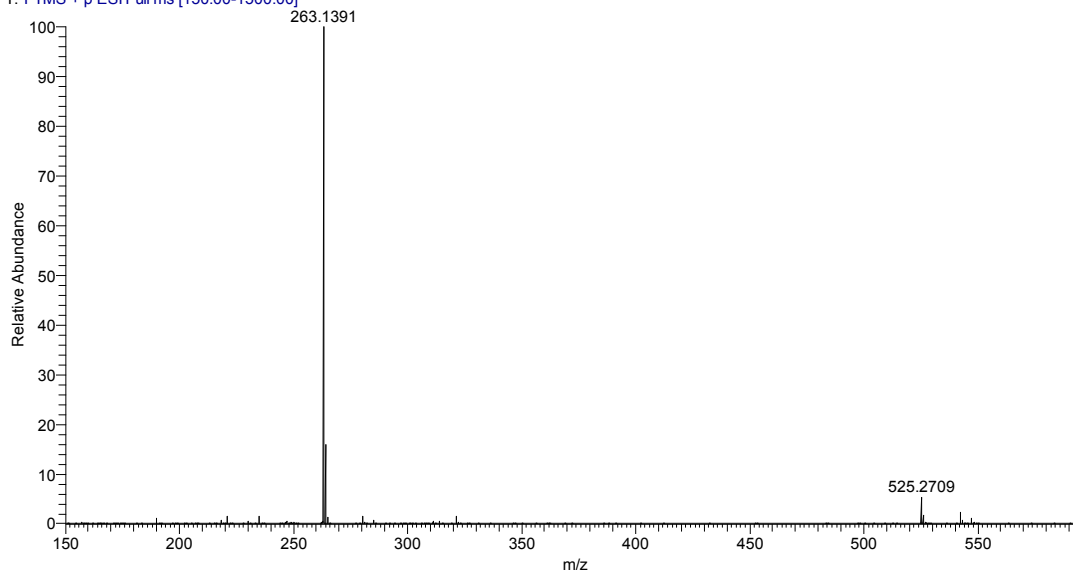
9 #74 RT: 0.78 AV: 1 NL: 7.88E9  
 T: FTMS + p ESI Full ms [150.00-1500.00]



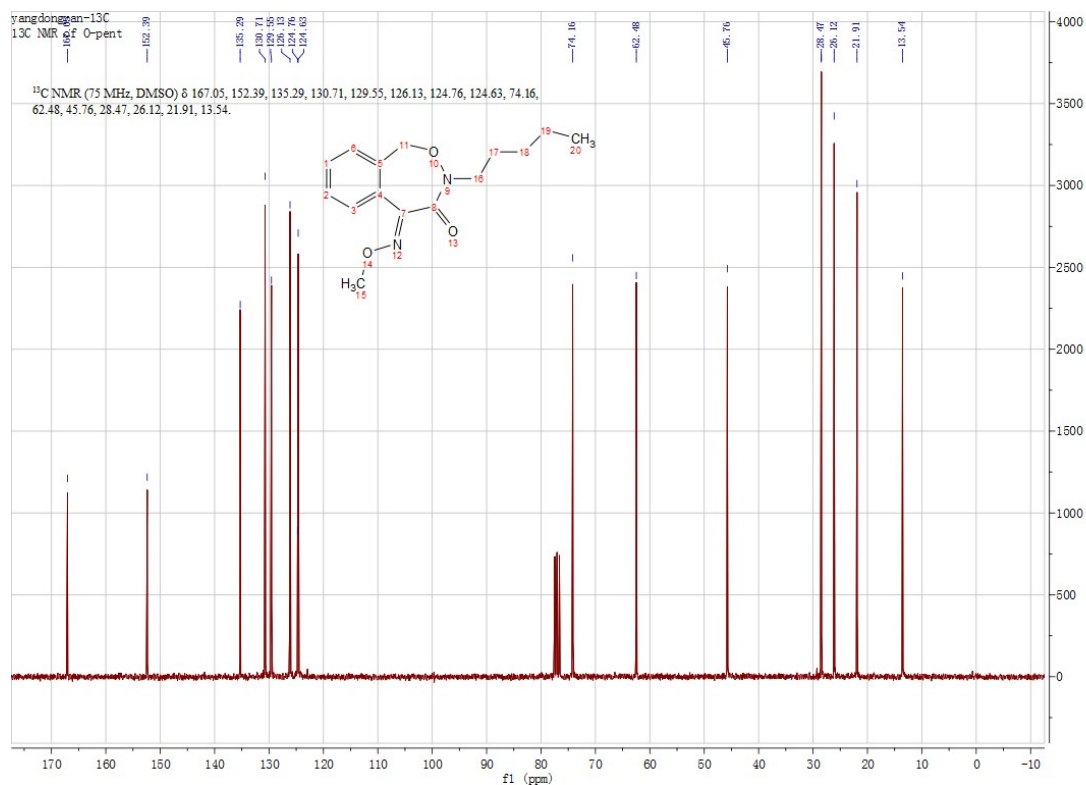
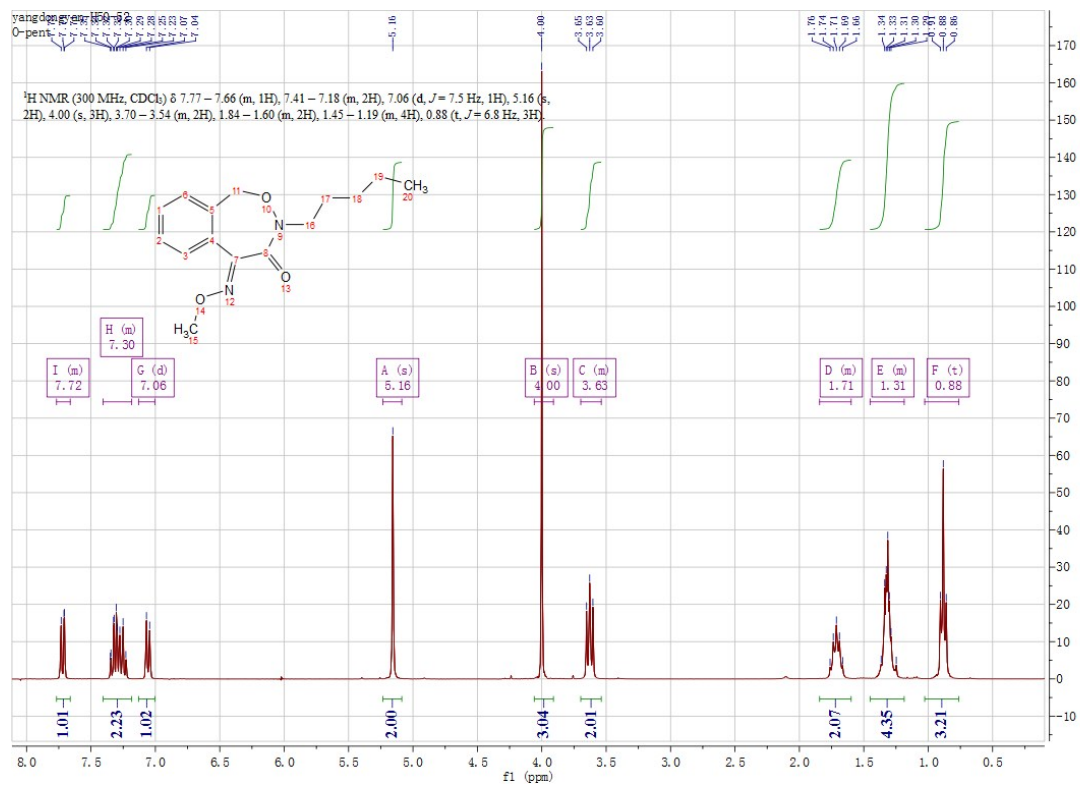
Data for (E)-3-butyl-5-(methoxyimino)-3,5-dihydrobenzo[e][1,2]oxazepin-4(1H)-one (**5-02**): yield 57 %; white solid; mp 54-55 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88 – 7.71 (m, 1H), 7.40 (ddd,  $J = 20.1, 9.9, 3.9$  Hz, 2H), 7.13 (d,  $J = 7.7$  Hz, 1H), 5.24 (s, 2H), 4.09 (s, 3H), 3.81 – 3.62 (m, 2H), 1.77 (dt,  $J = 15.0, 7.6$  Hz, 2H), 1.44 (dq,  $J = 14.7, 7.3$  Hz, 2H), 1.00 (t,  $J = 7.3$  Hz, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  167.23, 152.38, 135.28, 130.86, 129.59, 126.24, 124.88, 124.59, 74.28, 62.62, 45.69, 28.59, 19.68, 13.40. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{14}\text{H}_{18}\text{N}_2\text{O}_3$  ( $\text{M}+\text{H}$ ) $^+$  263.1390, found 263.1391.



13 #74 RT: 0.79 AV: 1 NL: 6.00E9  
T: FTMS + p ESI Full ms [150.00-1500.00]

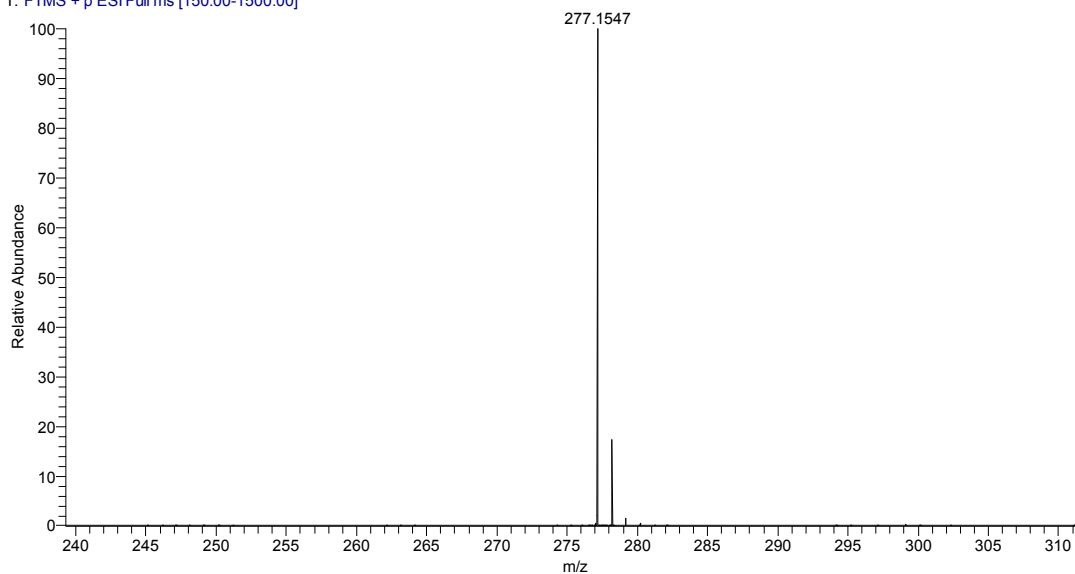


Data for (E)-5-(methoxyimino)-3-pentyl-3,5-dihydrobenzo[e][1,2]oxazepin-4(1H)-one (**5-03**): yield 69 %; colorless oil; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.77 – 7.66 (m, 1H), 7.41 – 7.18 (m, 2H), 7.06 (d, *J* = 7.5 Hz, 1H), 5.16 (s, 2H), 4.00 (s, 3H), 3.70 – 3.54 (m, 2H), 1.84 – 1.60 (m, 2H), 1.45 – 1.19 (m, 4H), 0.88 (t, *J* = 6.8 Hz, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 167.05, 152.39, 135.29, 130.71, 129.55, 126.13, 124.76, 124.63, 74.16, 62.48, 45.76, 28.47, 26.12, 21.91, 13.54. HRMS (ESI) *m/z* calcd for C<sub>15</sub>H<sub>20</sub>N<sub>2</sub>O<sub>3</sub> (M+H)<sup>+</sup> 277.1547, found 277.1547.

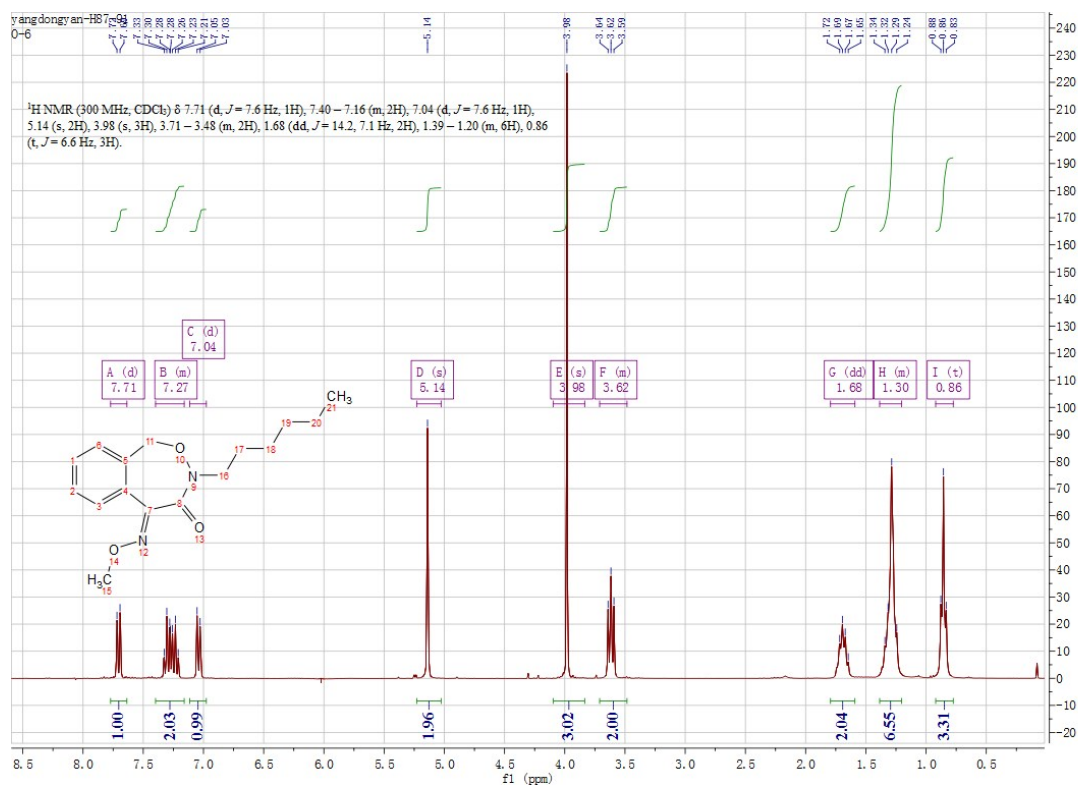


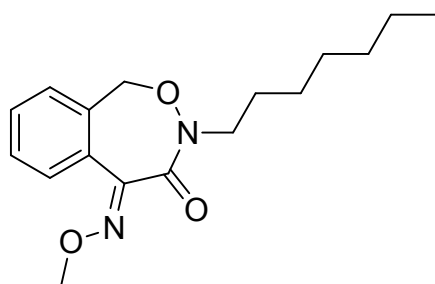
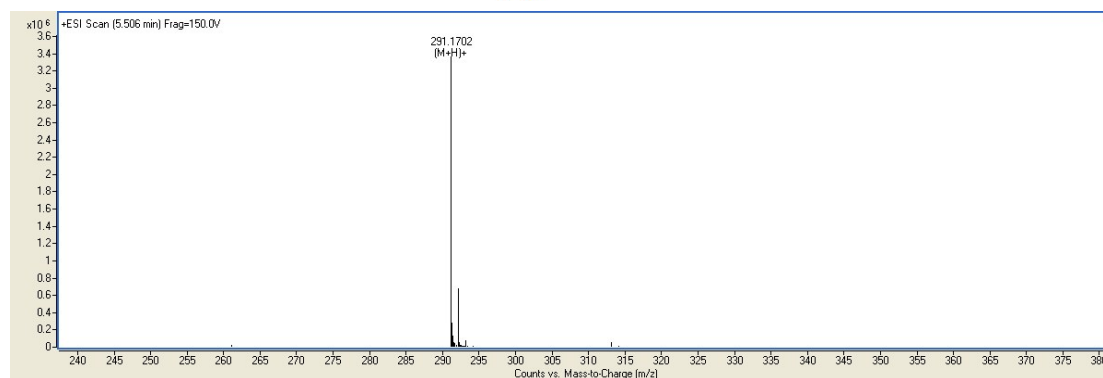
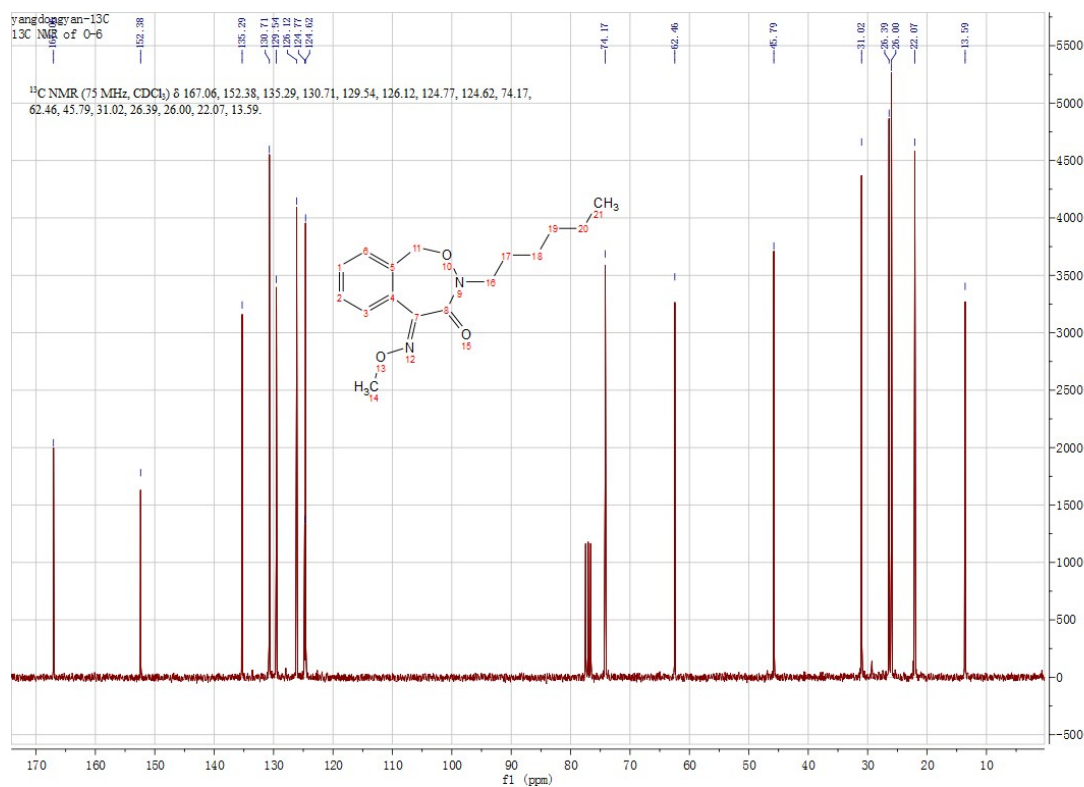


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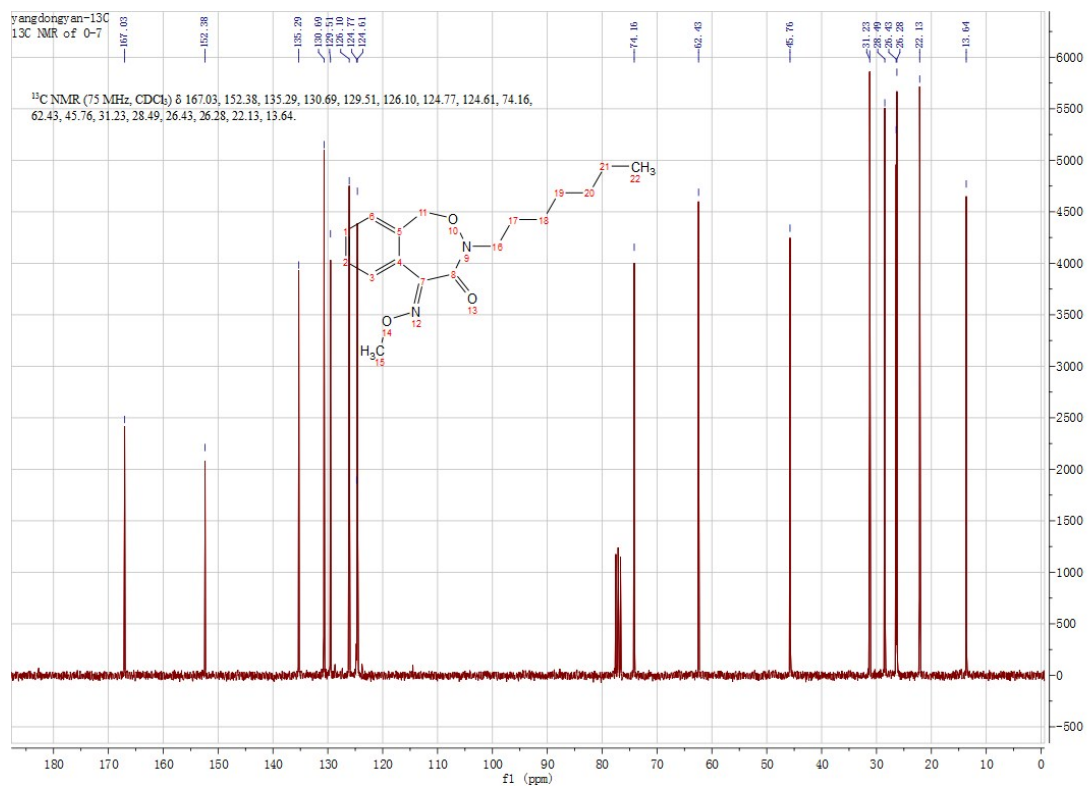
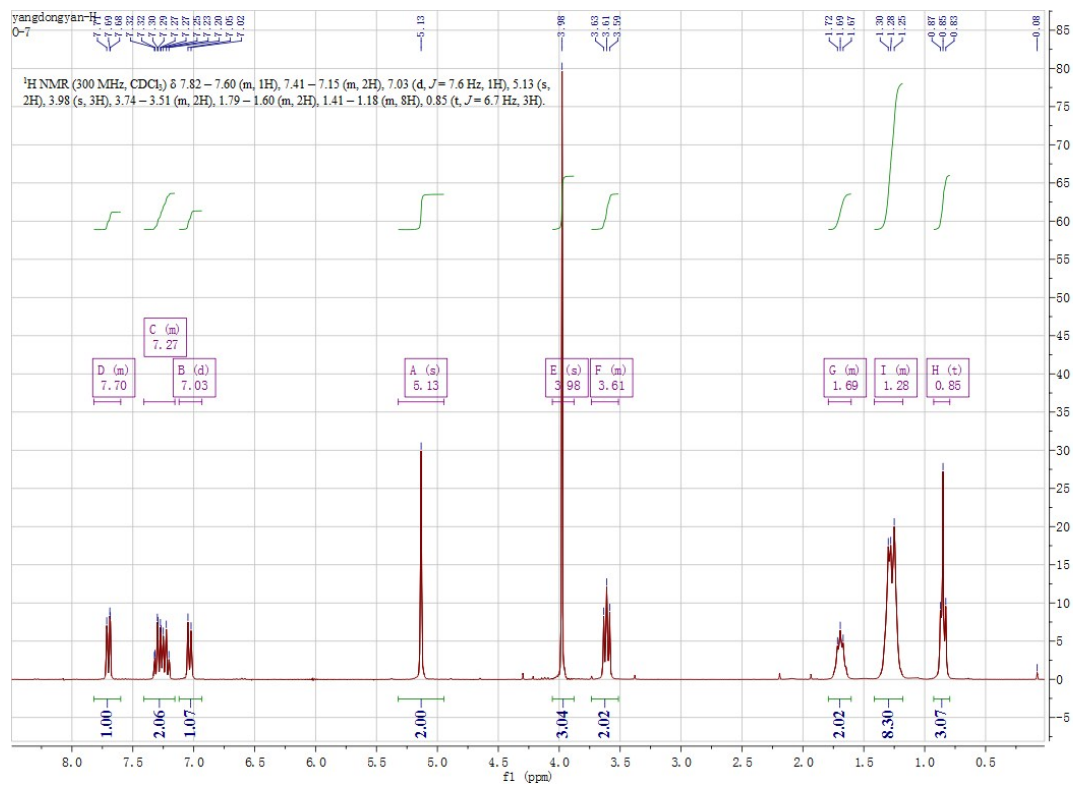


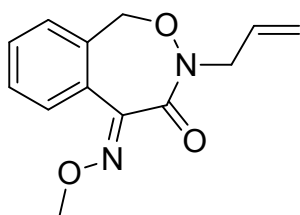
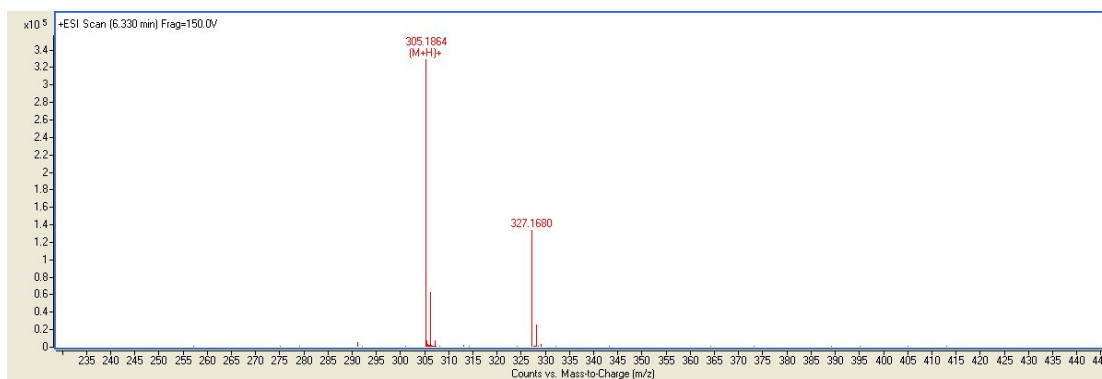
Data for (*E*)-3-hexyl-5-(methoxyimino)-3,5-dihydrobenzo[*e*][1,2]oxazepin-4(1*H*)-one (**5-04**): yield 75 %; colorless oil;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.71 (d,  $J = 7.6$  Hz, 1H), 7.40 – 7.16 (m, 2H), 7.04 (d,  $J = 7.6$  Hz, 1H), 5.14 (s, 2H), 3.98 (s, 3H), 3.71 – 3.48 (m, 2H), 1.68 (dd,  $J = 14.2, 7.1$  Hz, 2H), 1.39 – 1.20 (m, 6H), 0.86 (t,  $J = 6.6$  Hz, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  167.06, 152.38, 135.29, 130.71, 129.54, 126.12, 124.77, 124.62, 74.17, 62.46, 45.79, 31.02, 26.39, 26.00, 22.07, 13.59. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{16}\text{H}_{23}\text{N}_2\text{O}_3$  ( $\text{M}+\text{H}$ ) $^+$  291.1703, found 291.1702.



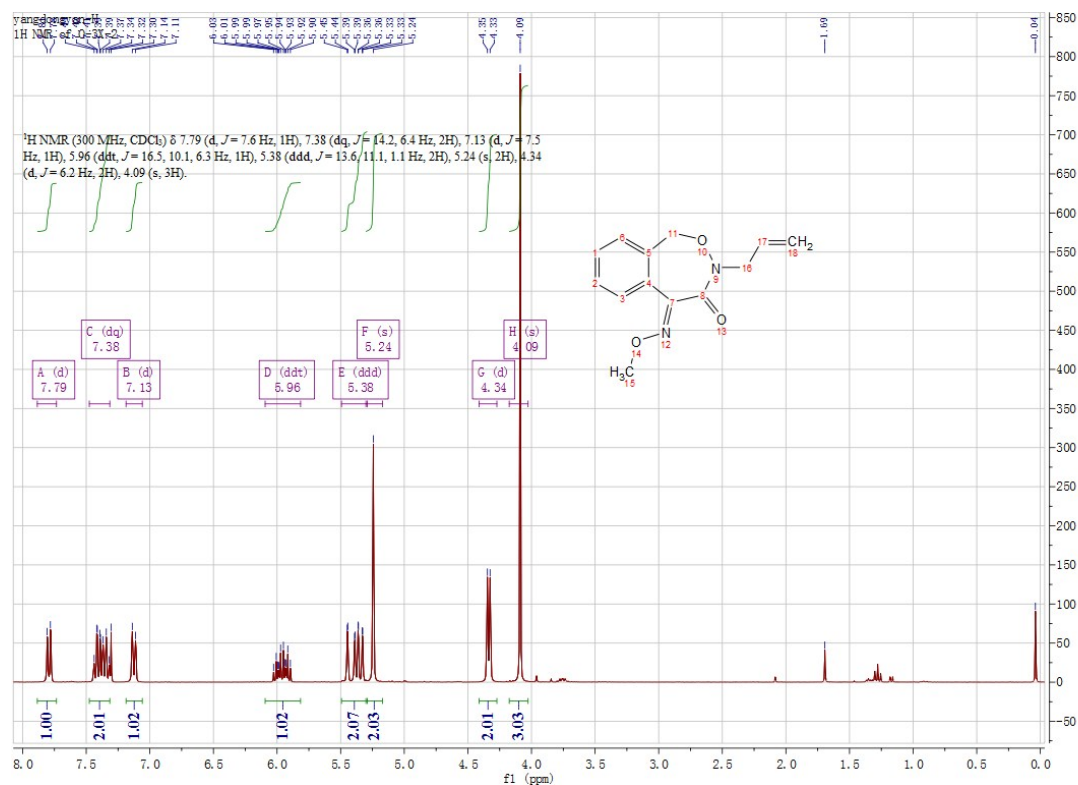


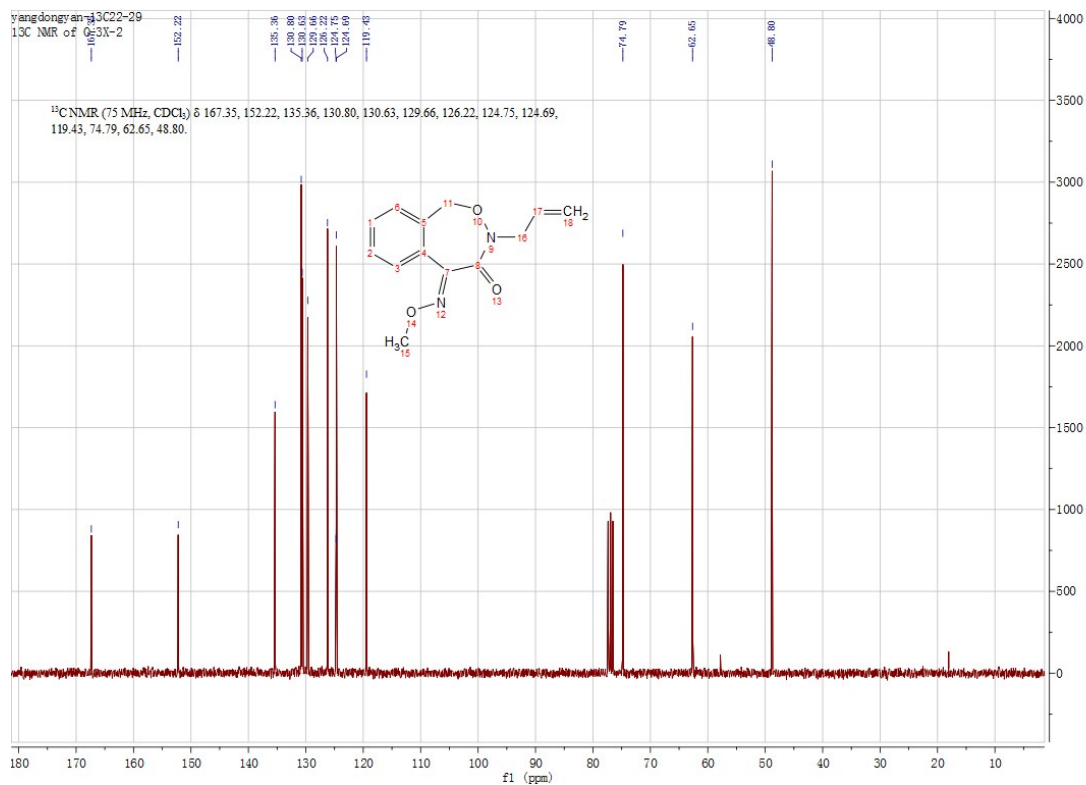
Data for *(E)*-3-heptyl-5-(methoxyimino)-3,5-dihydrobenzo[*e*][1,2]oxazepin-4(1H)-one (**5-05**): yield 73 %; colorless oil; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.82 – 7.60 (m, 1H), 7.41 – 7.15 (m, 2H), 7.03 (d, *J* = 7.6 Hz, 1H), 5.13 (s, 2H), 3.98 (s, 3H), 3.74 – 3.51 (m, 2H), 1.79 – 1.60 (m, 2H), 1.41 – 1.18 (m, 8H), 0.85 (t, *J* = 6.7 Hz, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 167.03, 152.38, 135.29, 130.69, 129.51, 126.10, 124.77, 124.61, 74.16, 62.43, 45.76, 31.23, 28.49, 26.43, 26.28, 22.13, 13.64. HRMS (ESI) *m/z* calcd for C<sub>17</sub>H<sub>25</sub>N<sub>2</sub>O<sub>3</sub> (M+H)<sup>+</sup> 305.1860, found 305.1864.



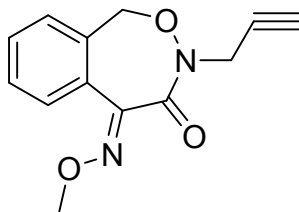
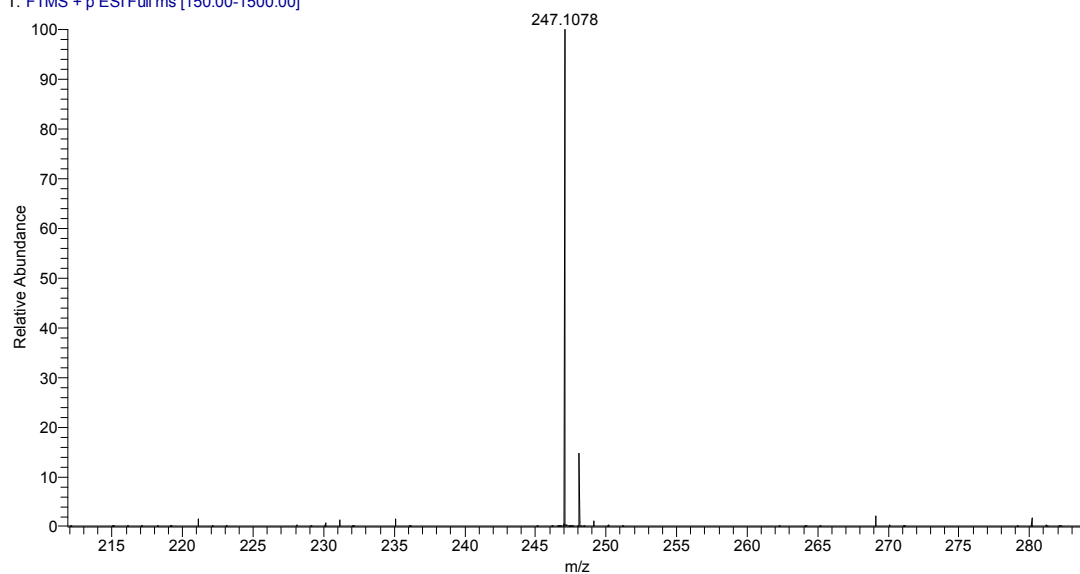


Data for (E)-3-allyl-5-(methoxyimino)-3,5-dihydrobenzo[e][1,2]oxazepin-4(1H)-one (**5-06**): yield 34 %; white solid; mp 62-63 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.79 (d, *J* = 7.6 Hz, 1H), 7.38 (dq, *J* = 14.2, 6.4 Hz, 2H), 7.13 (d, *J* = 7.5 Hz, 1H), 5.96 (ddt, *J* = 16.5, 10.1, 6.3 Hz, 1H), 5.38 (ddd, *J* = 13.6, 11.1, 1.1 Hz, 2H), 5.24 (s, 2H), 4.34 (d, *J* = 6.2 Hz, 2H), 4.09 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 167.35, 152.22, 135.36, 130.80, 130.63, 129.66, 126.22, 124.75, 124.69, 119.43, 74.79, 62.65, 48.80. HRMS (ESI) *m/z* calcd for C<sub>13</sub>H<sub>14</sub>N<sub>2</sub>O<sub>3</sub> (M+H)<sup>+</sup> 247.1077, found 247.1078.



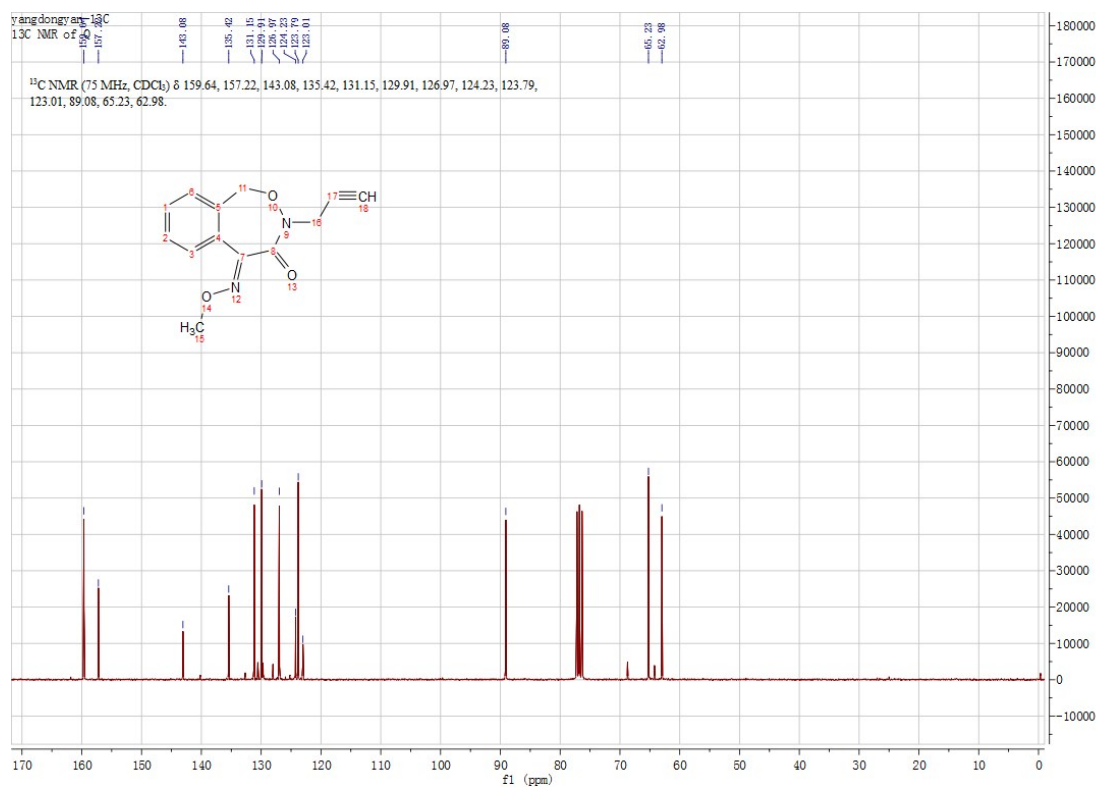
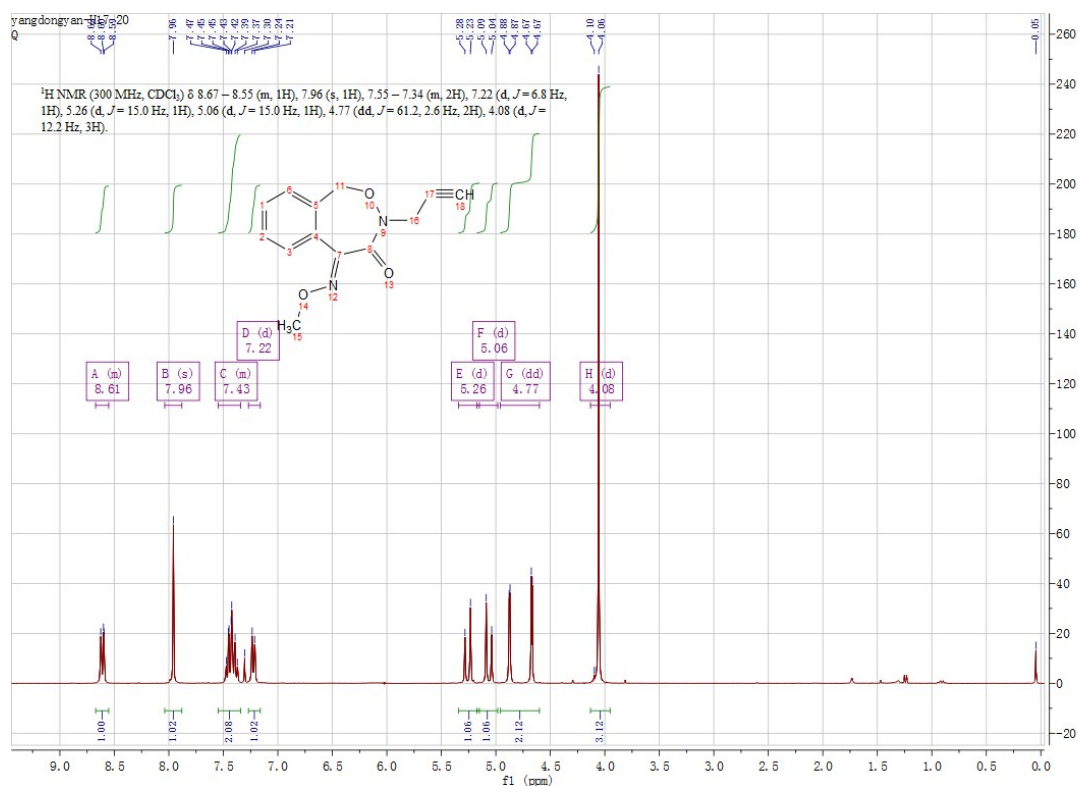


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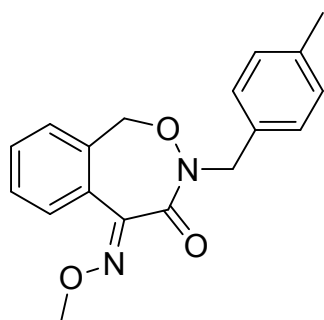
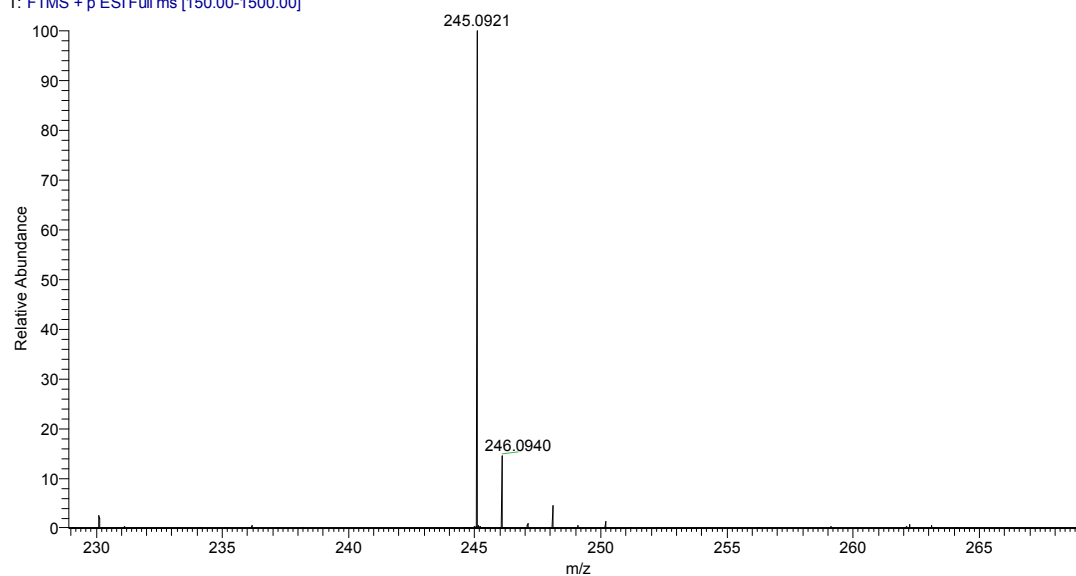


Data for (E)-5-(methoxyimino)-3-(prop-2-yn-1-yl)-3,5-dihydrobenzo[e][1,2]oxazepin-4(1H)-one (5-07): yield 52.5 %; yellowish solid; mp 82-83 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.67 – 8.55 (m,

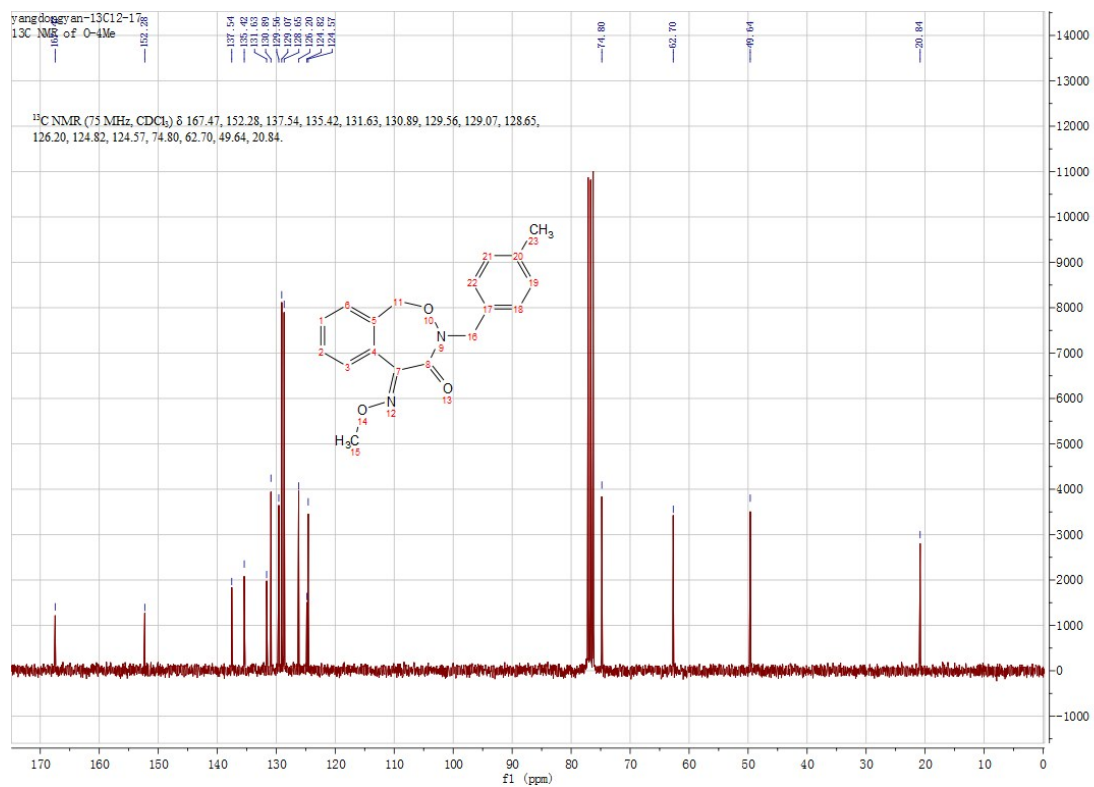
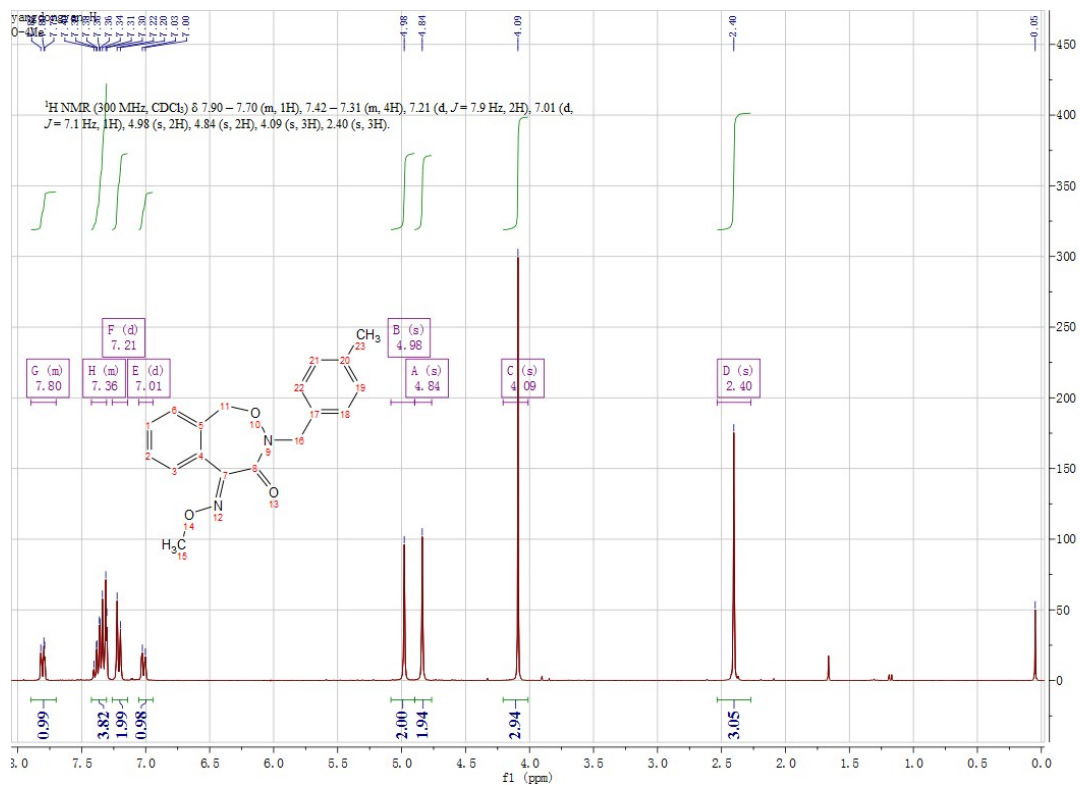
1H), 7.96 (s, 1H), 7.55 – 7.34 (m, 2H), 7.22 (d,  $J = 6.8$  Hz, 1H), 5.26 (d,  $J = 15.0$  Hz, 1H), 5.06 (d,  $J = 15.0$  Hz, 1H), 4.77 (dd,  $J = 61.2, 2.6$  Hz, 2H), 4.08 (d,  $J = 12.2$  Hz, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  159.64, 157.22, 143.08, 135.42, 131.15, 129.91, 126.97, 124.23, 123.79, 123.01, 89.08, 65.23, 62.98. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{13}\text{H}_{12}\text{N}_2\text{O}_3$  (M+H) $^+$  245.0921, found 245.0921.



4 #72 RT: 0.76 AV: 1 NL: 2.59E9  
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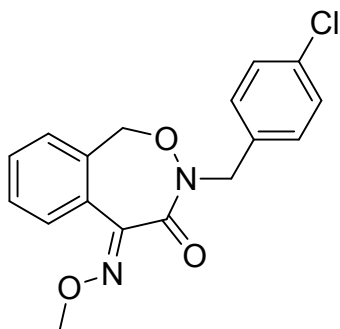
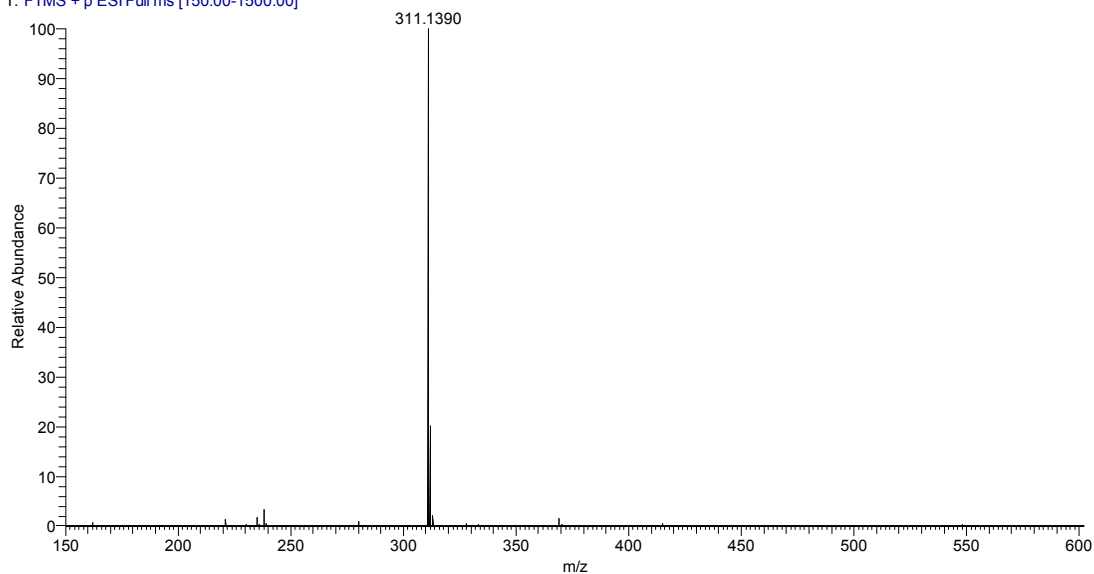


Data for (E)-5-(methoxyimino)-3-(4-methylbenzyl)-3,5-dihydrobenzo[e][1,2]oxazepin-4(1H)-one (**5-08**): yield 50.9 %; white solid; mp 72-74 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.90 – 7.70 (m, 1H), 7.42 – 7.31 (m, 4H), 7.21 (d,  $J = 7.9$  Hz, 2H), 7.01 (d,  $J = 7.1$  Hz, 1H), 4.98 (s, 2H), 4.84 (s, 2H), 4.09 (s, 3H), 2.40 (s, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  167.47, 152.28, 137.54, 135.42, 131.63, 130.89, 129.56, 129.07, 128.65, 126.20, 124.82, 124.57, 74.80, 62.70, 49.64, 20.84. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_3$  ( $\text{M}+\text{H}$ ) $^+$  311.1390, found 311.1390.

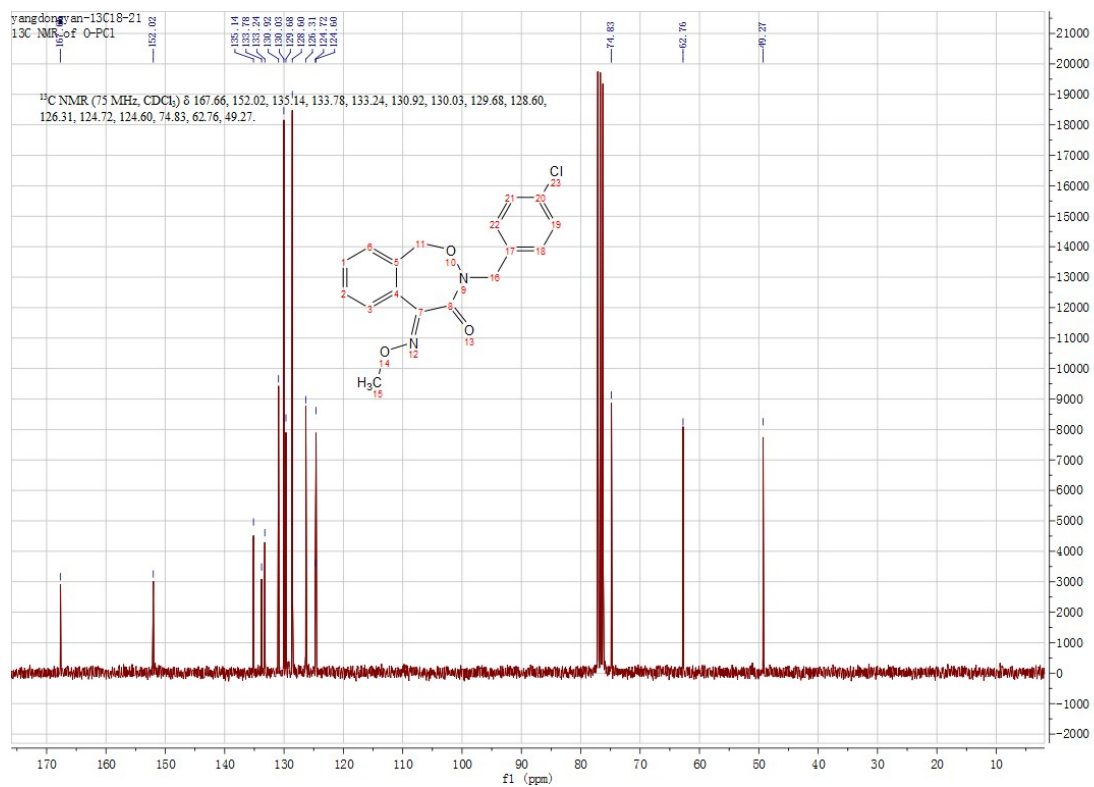
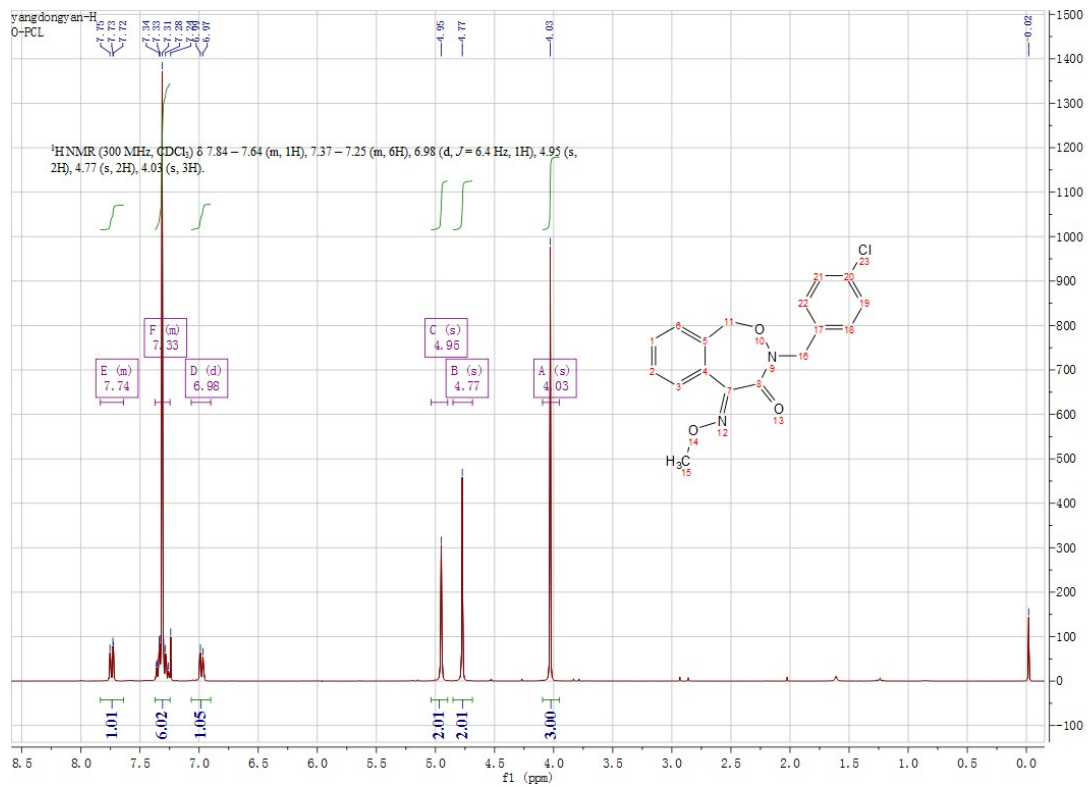




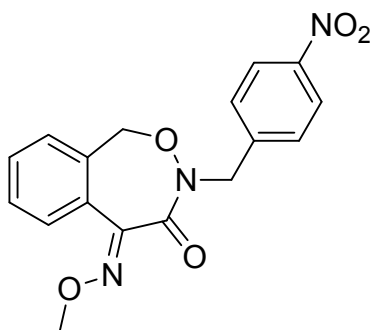
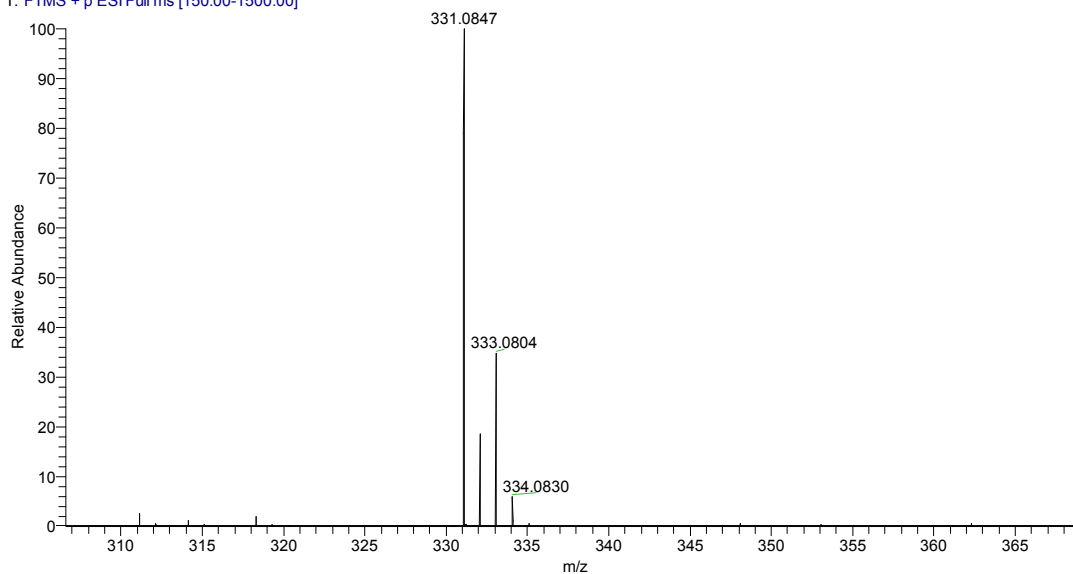
7 #74 RT: 0.78 AV: 1 NL: 1.10E10  
T: FTMS + p ESI Full ms [150.00-1500.00]



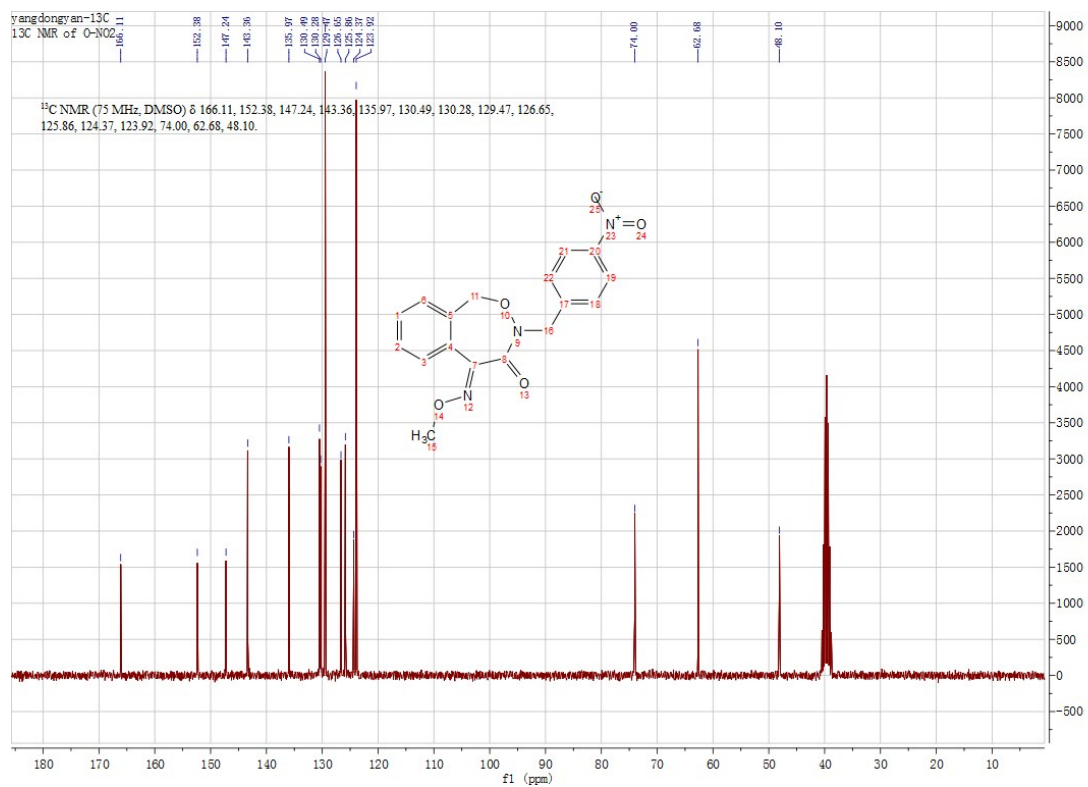
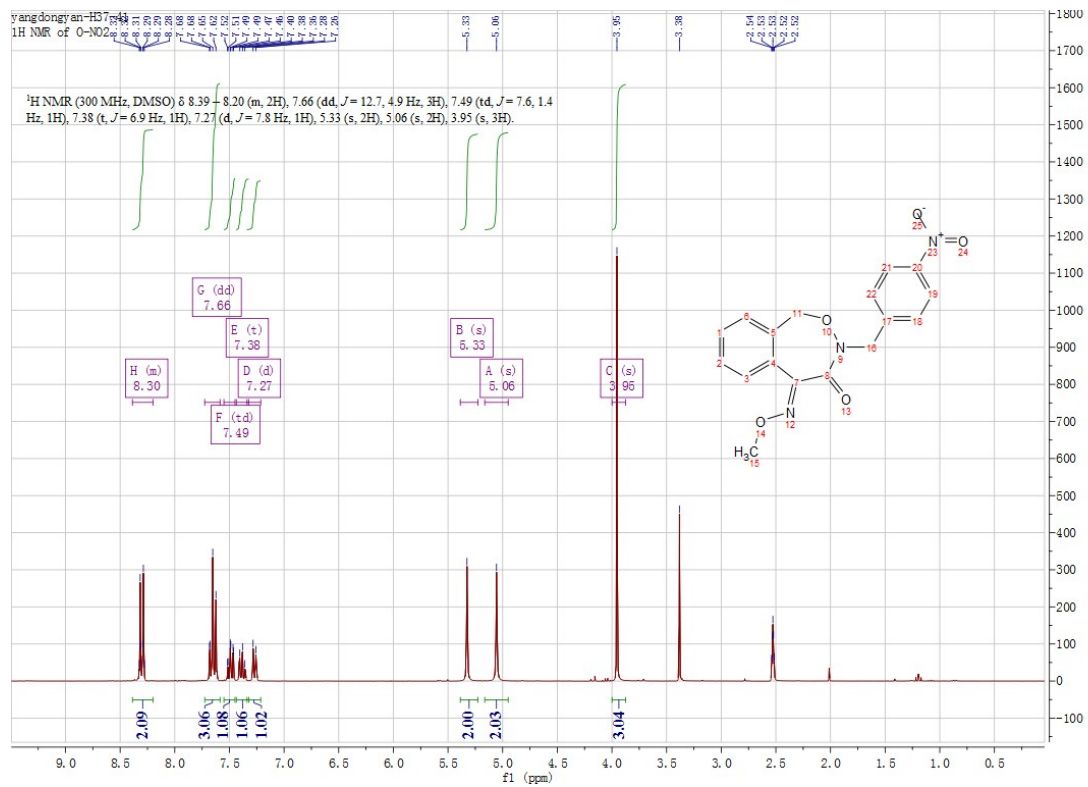
Data for (E)-3-(4-chlorobenzyl)-5-(methoxyimino)-3,5-dihydrobenzo[e][1,2]oxazepin-4(1H)-one (**5-09**): yield 75 %; white solid; mp 93-94 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.84 – 7.64 (m, 1H), 7.37 – 7.25 (m, 6H), 6.98 (d,  $J$  = 6.4 Hz, 1H), 4.95 (s, 2H), 4.77 (s, 2H), 4.03 (s, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  167.66, 152.02, 135.14, 133.78, 133.24, 130.92, 130.03, 129.68, 128.60, 126.31, 124.72, 124.60, 74.83, 62.76, 49.27. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{17}\text{H}_{15}\text{ClN}_2\text{O}_3$  ( $\text{M}+\text{H}$ ) $^+$  331.0844, found 331.0847.



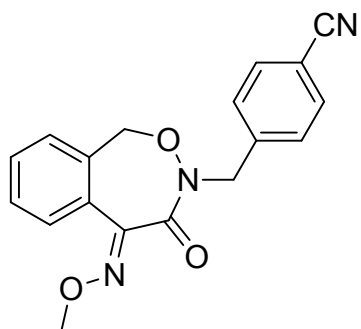
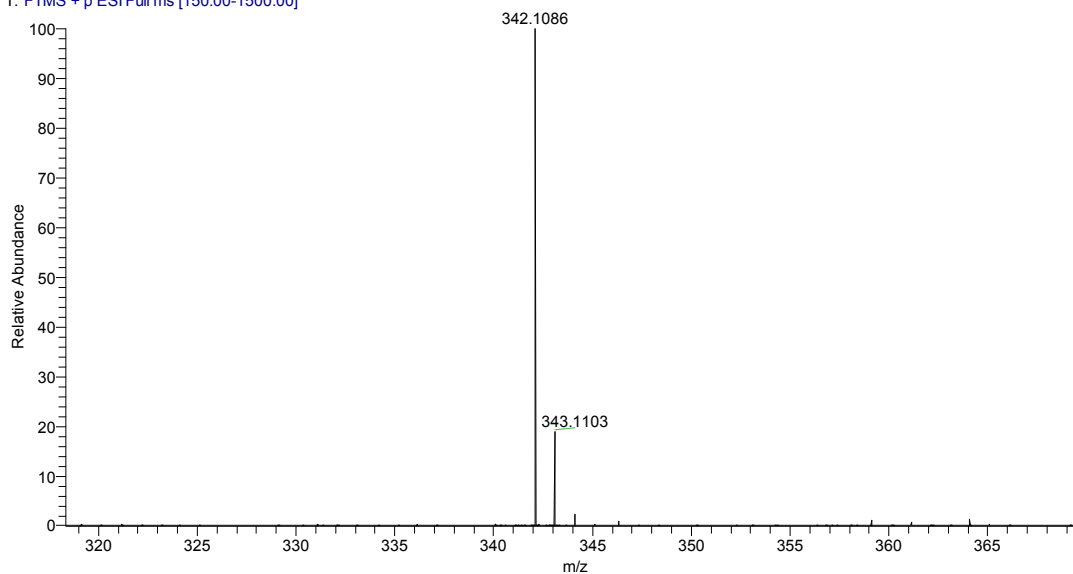
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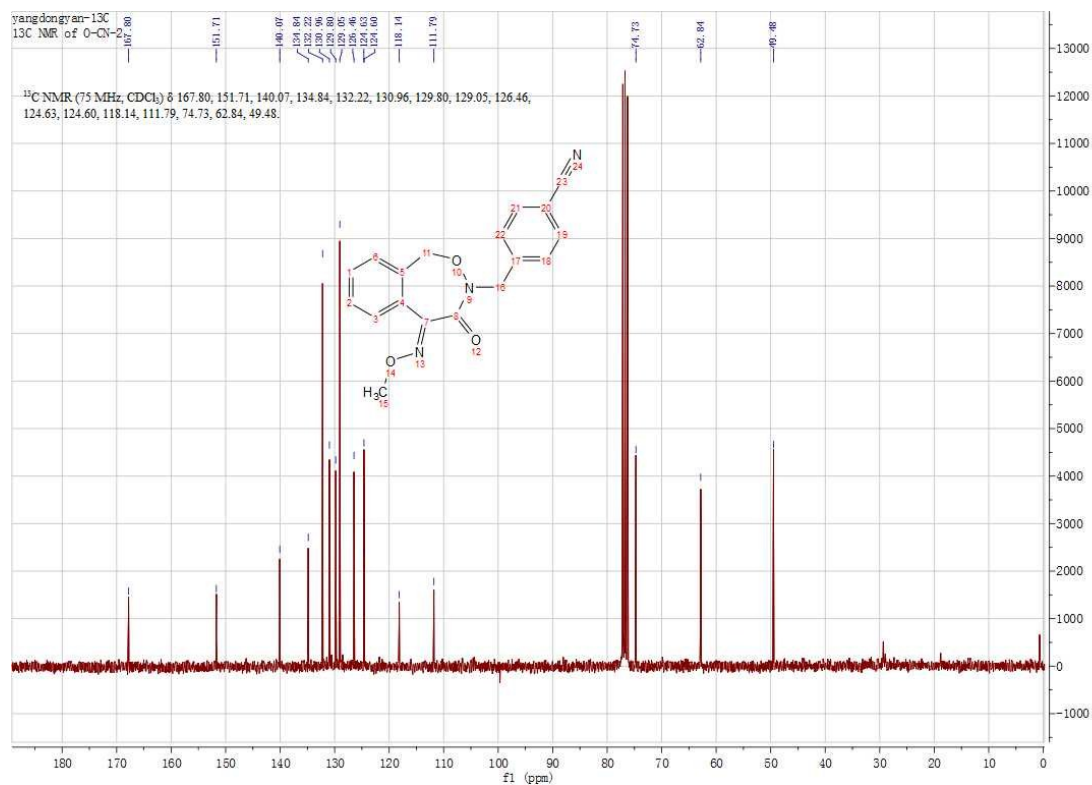
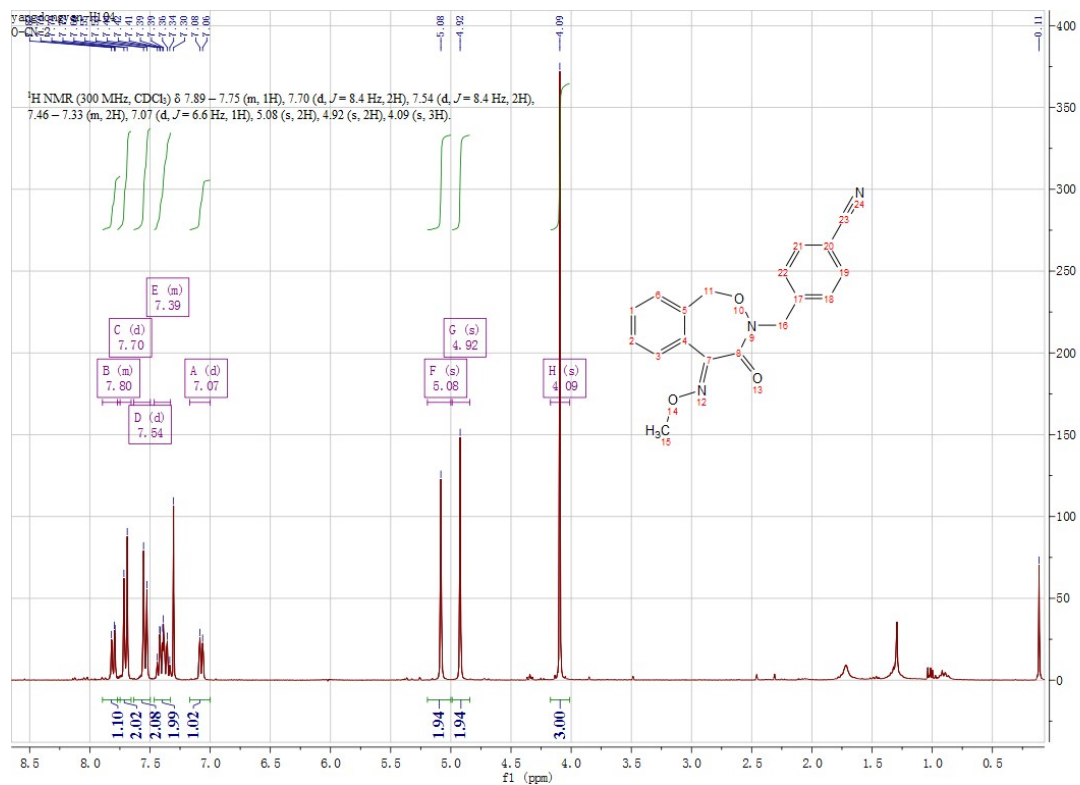
Data for (E)-5-(methoxyimino)-3-(4-nitrobenzyl)-3,5-dihydrobenzo[e][1,2]oxazepin-4(1H)-one (**5-10**): yield 56 %; yellowish solid; mp 92-93 °C;  $^1\text{H}$  NMR (300 MHz, DMSO)  $\delta$  8.39 – 8.20 (m, 2H), 7.66 (dd,  $J$  = 12.7, 4.9 Hz, 3H), 7.49 (td,  $J$  = 7.6, 1.4 Hz, 1H), 7.38 (t,  $J$  = 6.9 Hz, 1H), 7.27 (d,  $J$  = 7.8 Hz, 1H), 5.33 (s, 2H), 5.06 (s, 2H), 3.95 (s, 3H).  $^{13}\text{C}$  NMR (75 MHz, DMSO)  $\delta$  166.11, 152.38, 147.24, 143.36, 135.97, 130.49, 130.28, 129.47, 126.65, 125.86, 124.37, 123.92, 74.00, 62.68, 48.10. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{17}\text{H}_{15}\text{N}_3\text{O}_5$  ( $\text{M}+\text{H}$ ) $^+$  342.1086, found 342.1084.

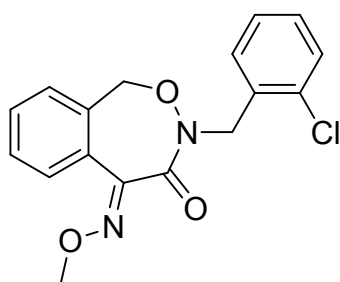
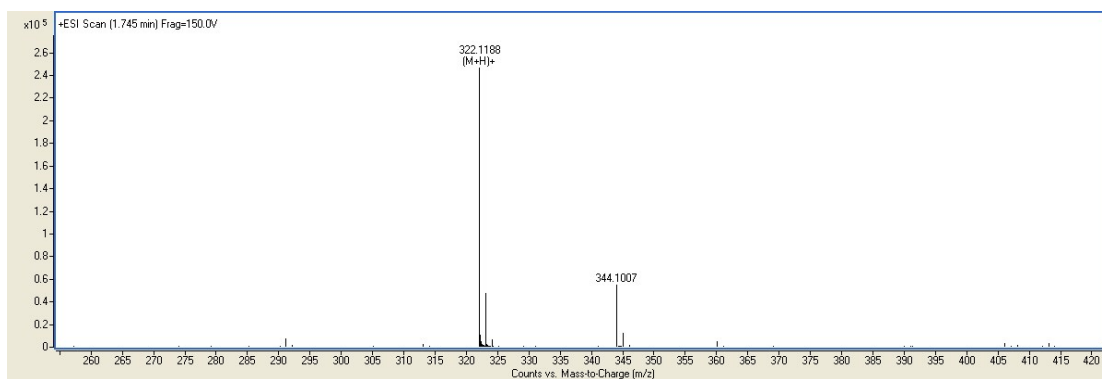


10 #68 RT: 0.72 AV: 1 NL: 6.14E8  
T: FTMS + p ESI Full ms [150.00-1500.00]

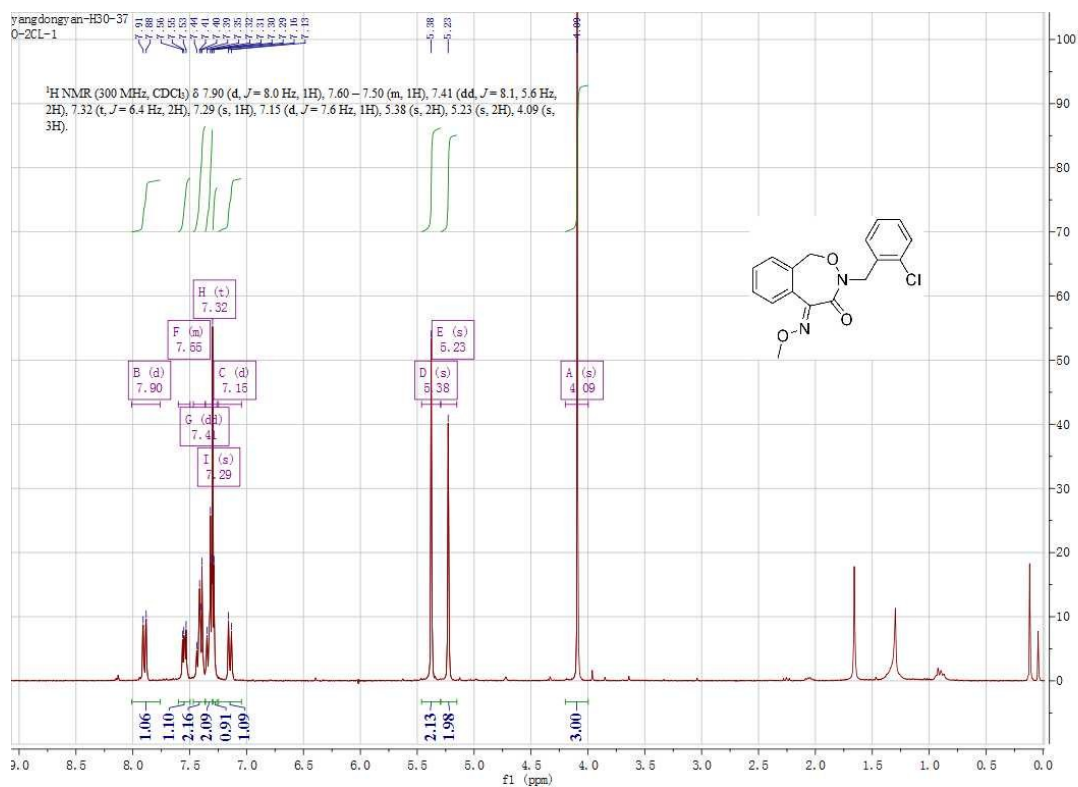


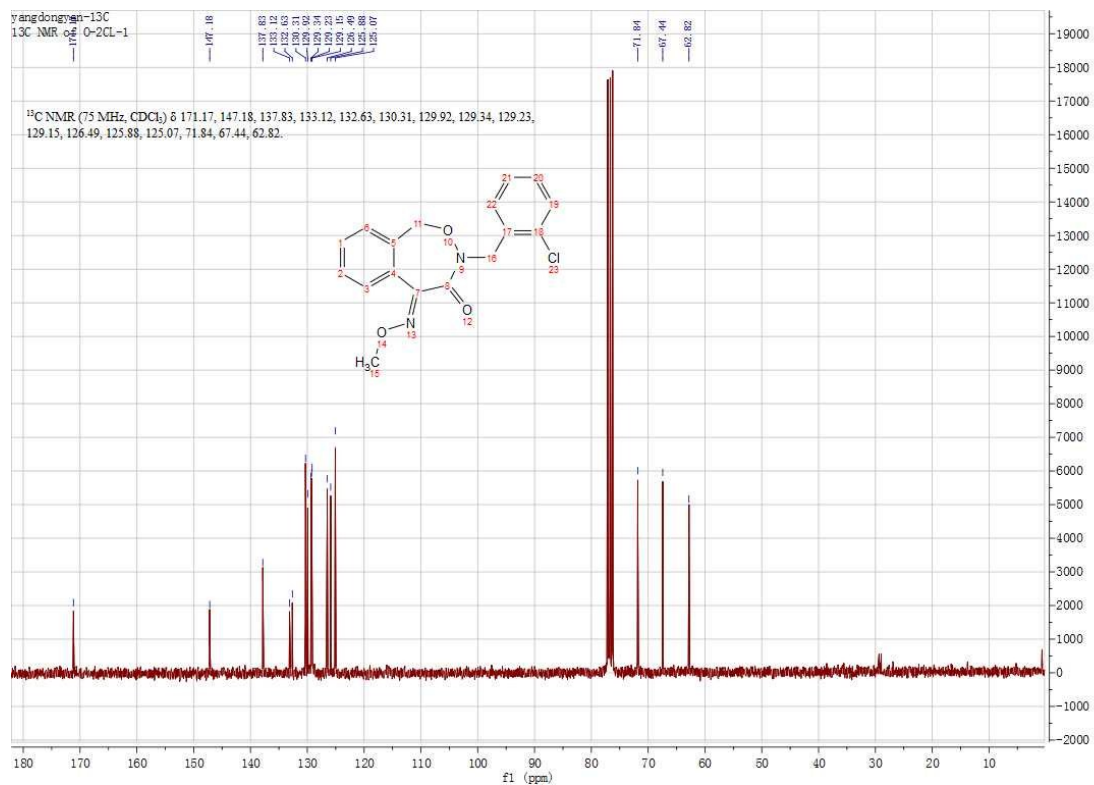
Data for (E)-4-((5-(methoxyimino)-4-oxo-4,5-dihydrobenzo[e][1,2]oxazepin-3(1H)-yl)methyl)benzonitrile (**5-11**). Yellowish oil; yield, 26%.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.89 – 7.75 (m, 1H), 7.70 (d,  $J$  = 8.4 Hz, 2H), 7.54 (d,  $J$  = 8.4 Hz, 2H), 7.46 – 7.33 (m, 2H), 7.07 (d,  $J$  = 6.6 Hz, 1H), 5.08 (s, 2H), 4.92 (s, 2H), 4.09 (s, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  167.80, 151.71, 140.07, 134.84, 132.22, 130.96, 129.80, 129.05, 126.46, 124.63, 124.60, 118.14, 111.79, 74.73, 62.84, 49.48. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{18}\text{H}_{16}\text{N}_3\text{O}_3$  ( $\text{M}+\text{H}$ ) $^+$  322.1186, found 322.1185.



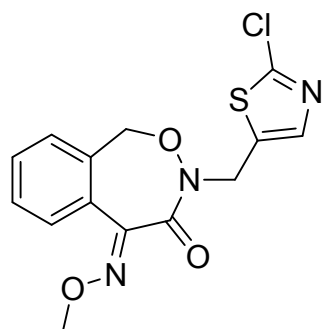
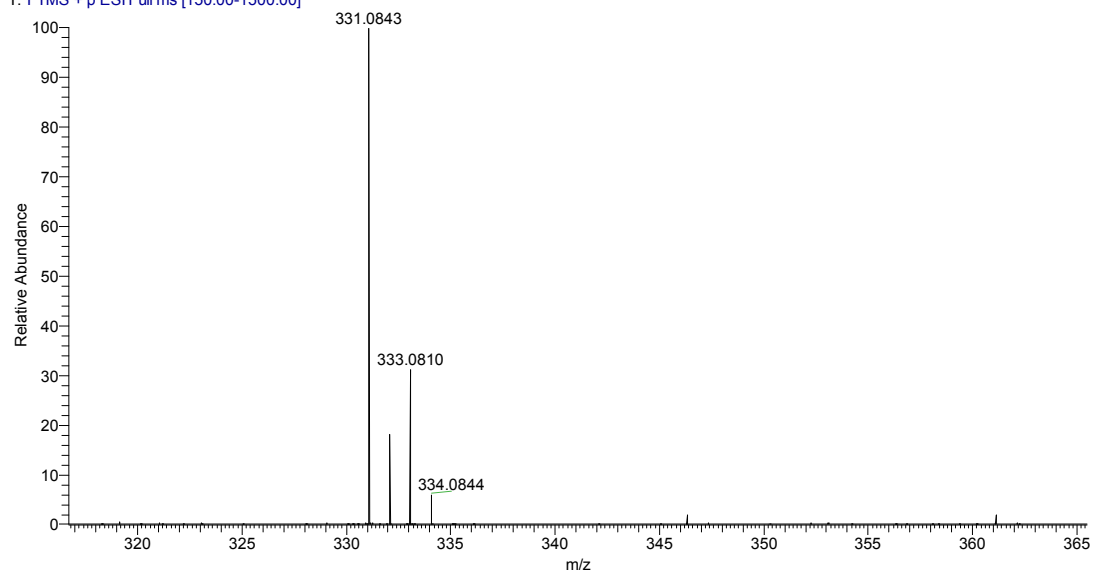


Data for (E)-3-(2-chlorobenzyl)-5-(methoxyimino)-3,5-dihydrobenzo[e][1,2]oxazepin-4(1H)-one (**5-12**): yield 24 %; white solid; mp 69-70°C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.90 (d, *J* = 8.0 Hz, 1H), 7.60 – 7.50 (m, 1H), 7.41 (dd, *J* = 8.1, 5.6 Hz, 2H), 7.32 (t, *J* = 6.4 Hz, 2H), 7.29 (s, 1H), 7.15 (d, *J* = 7.6 Hz, 1H), 5.38 (s, 2H), 5.23 (s, 2H), 4.09 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 171.17, 147.18, 137.83, 133.12, 132.63, 130.31, 129.92, 129.34, 129.23, 129.15, 126.49, 125.88, 125.07, 71.84, 67.44, 62.82. HRMS (ESI) *m/z* calcd for C<sub>17</sub>H<sub>15</sub>ClN<sub>2</sub>O<sub>3</sub> (M+H)<sup>+</sup> 331.0844, found 331.0843.





12\_160522125312 #72 RT: 0.76 AV: 1 NL: 1.91E8  
 T: FTMS + p ESI Full ms [150.00-1500.00]



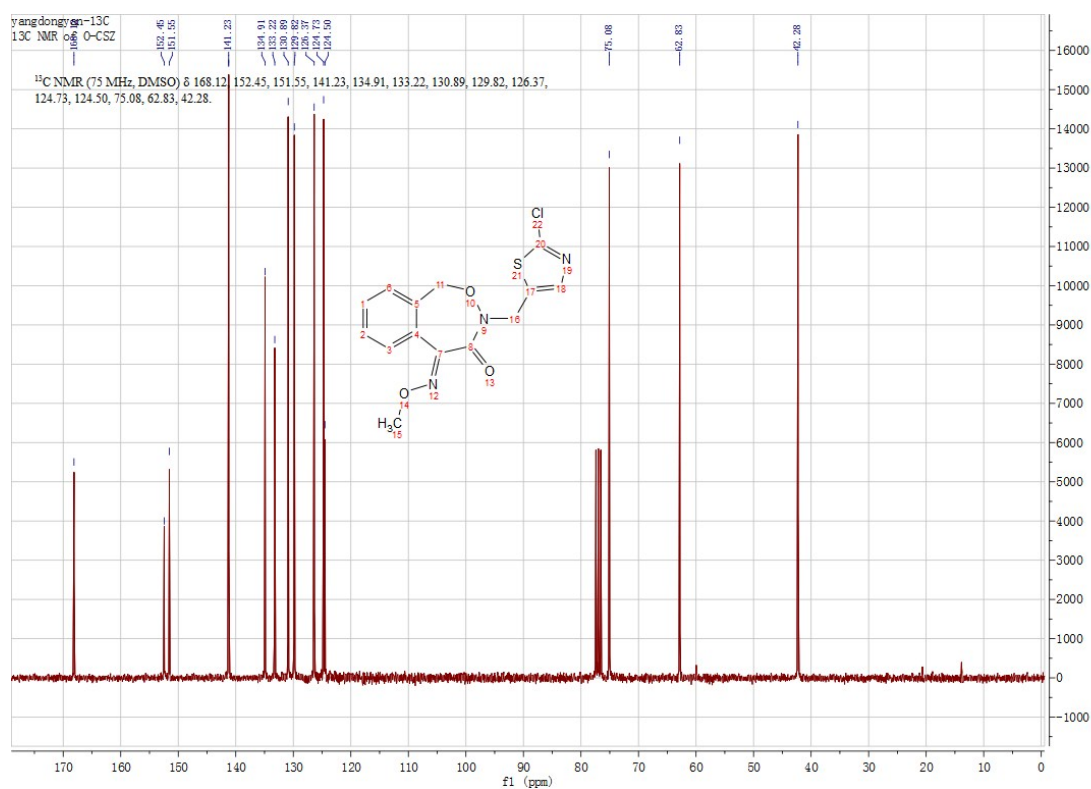
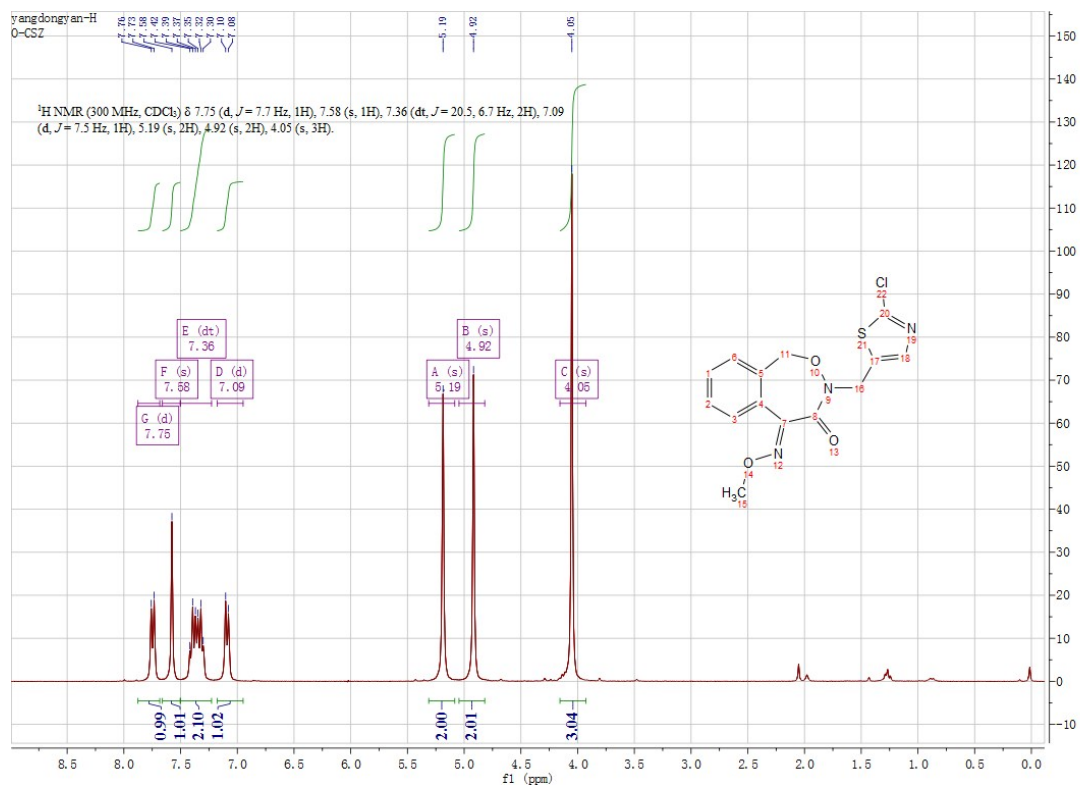
Data

for

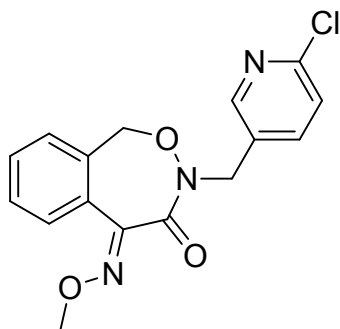
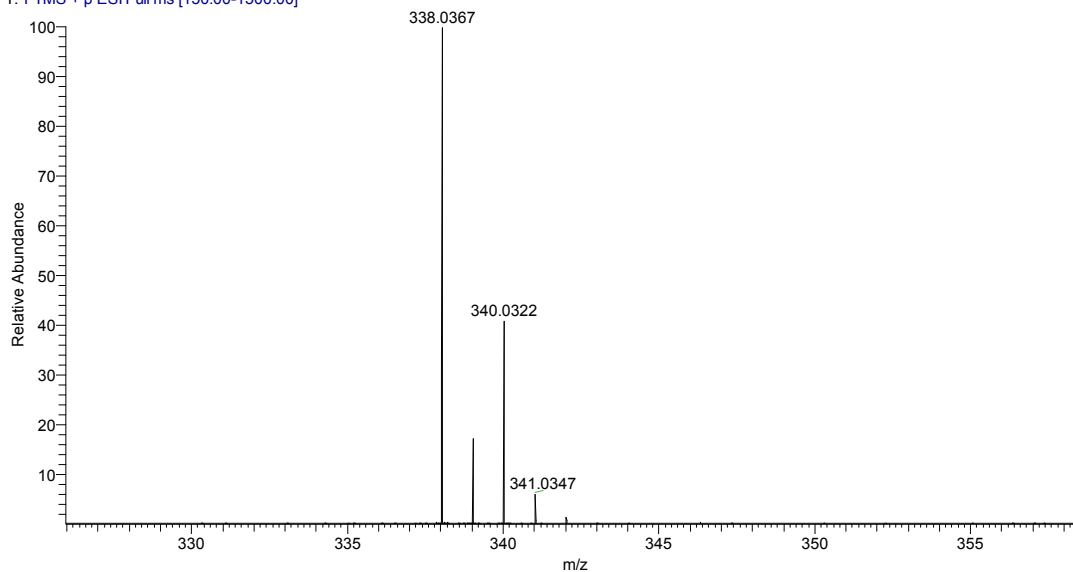
(E)-3-((2-chlorothiazol-5-yl)methyl)-5-(methoxyimino)-3,5-



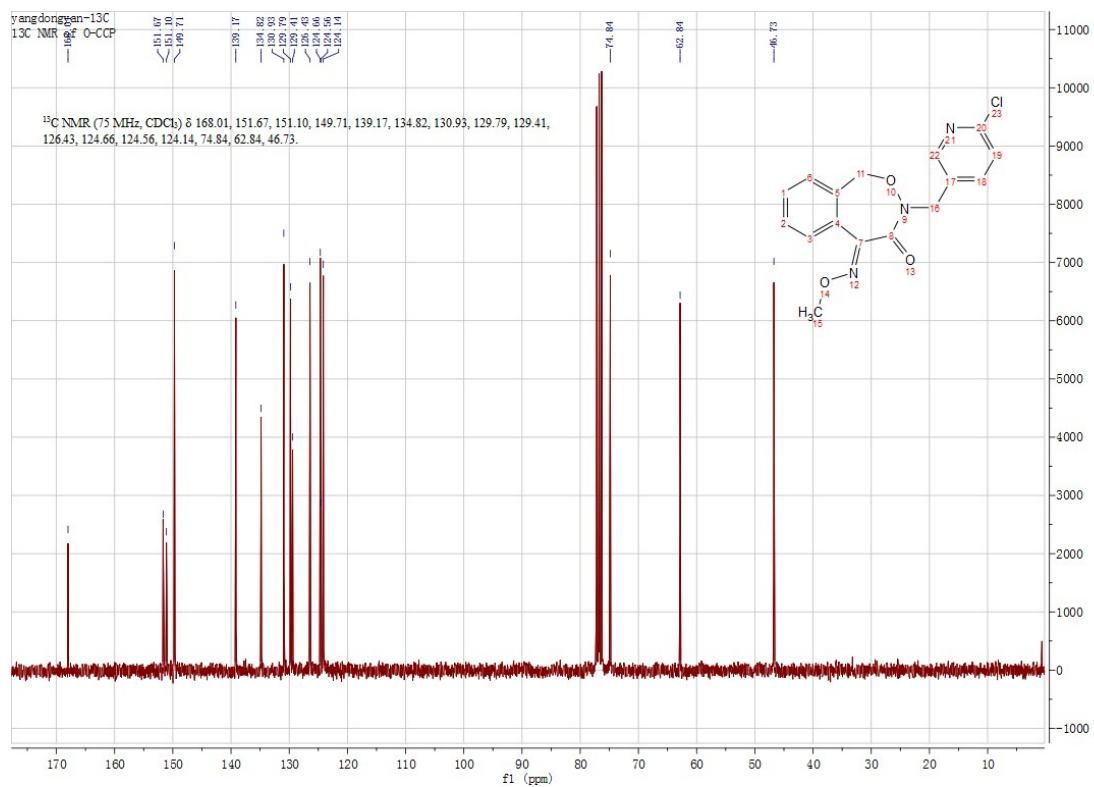
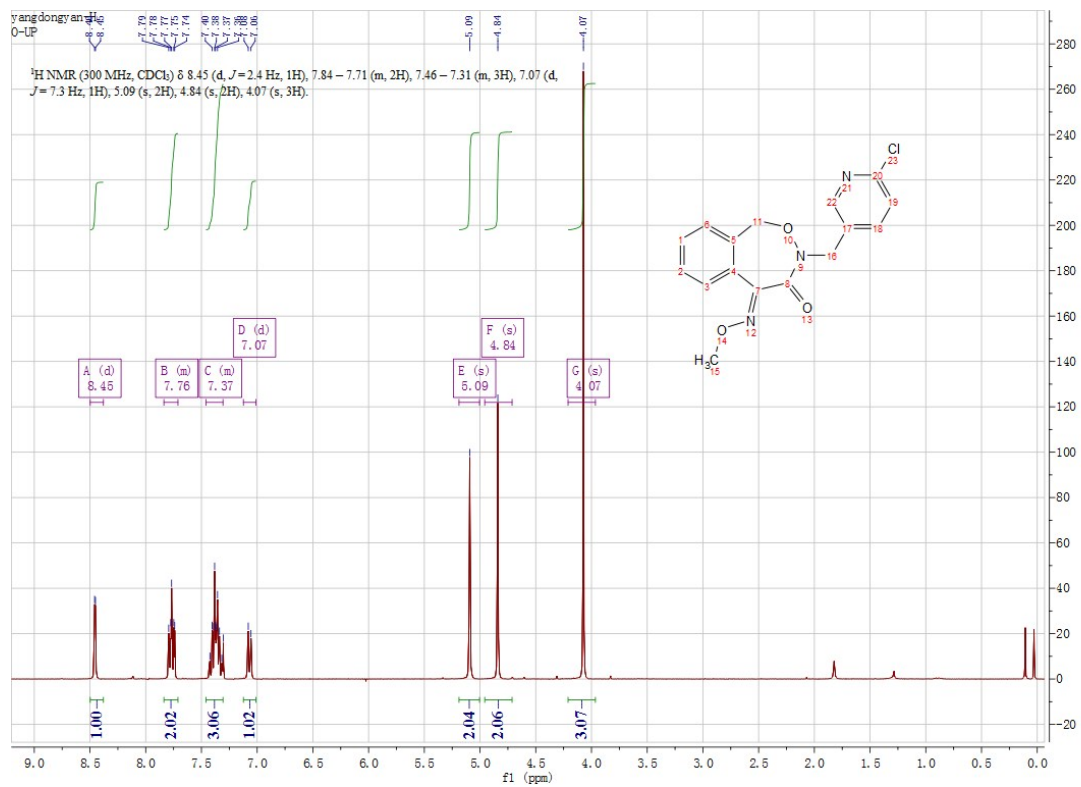
dihydrobenzo[e][1,2]oxazepin-4(1H)-one (**5-13**): yield 66 %; yellowish solid; mp 109-111 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.75 (d,  $J = 7.7$  Hz, 1H), 7.58 (s, 1H), 7.36 (dt,  $J = 20.5, 6.7$  Hz, 2H), 7.09 (d,  $J = 7.5$  Hz, 1H), 5.19 (s, 2H), 4.92 (s, 2H), 4.05 (s, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  168.12, 152.45, 151.55, 141.23, 134.91, 133.22, 130.89, 129.82, 126.37, 124.73, 124.50, 75.08, 62.83, 42.28. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{14}\text{H}_{12}\text{ClN}_3\text{O}_3\text{S}$  ( $\text{M}+\text{H}$ ) $^+$  338.0361, found 338.0367.

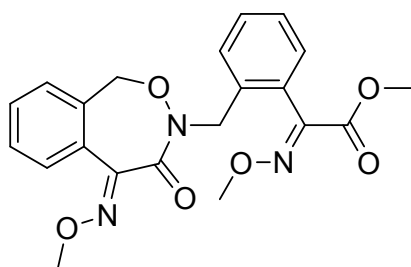
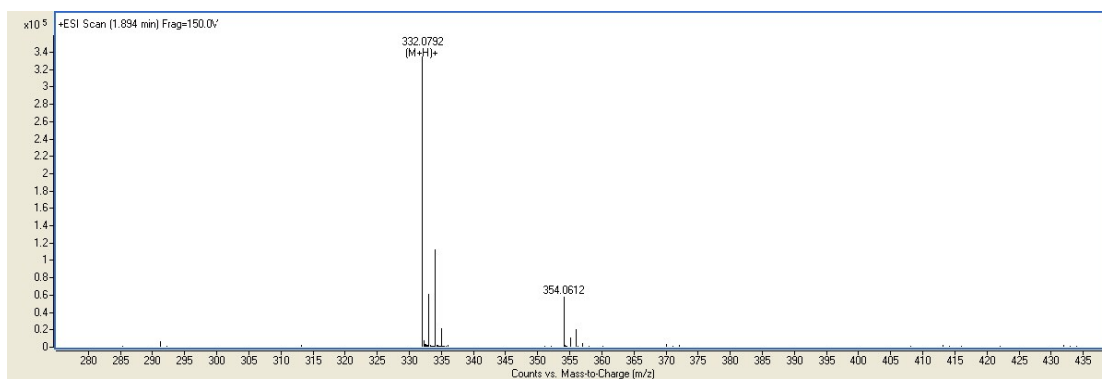


15 #76 RT: 0.80 AV: 1 NL: 1.40E9  
T: FTMS + p ESI Full ms [150.00-1500.00]

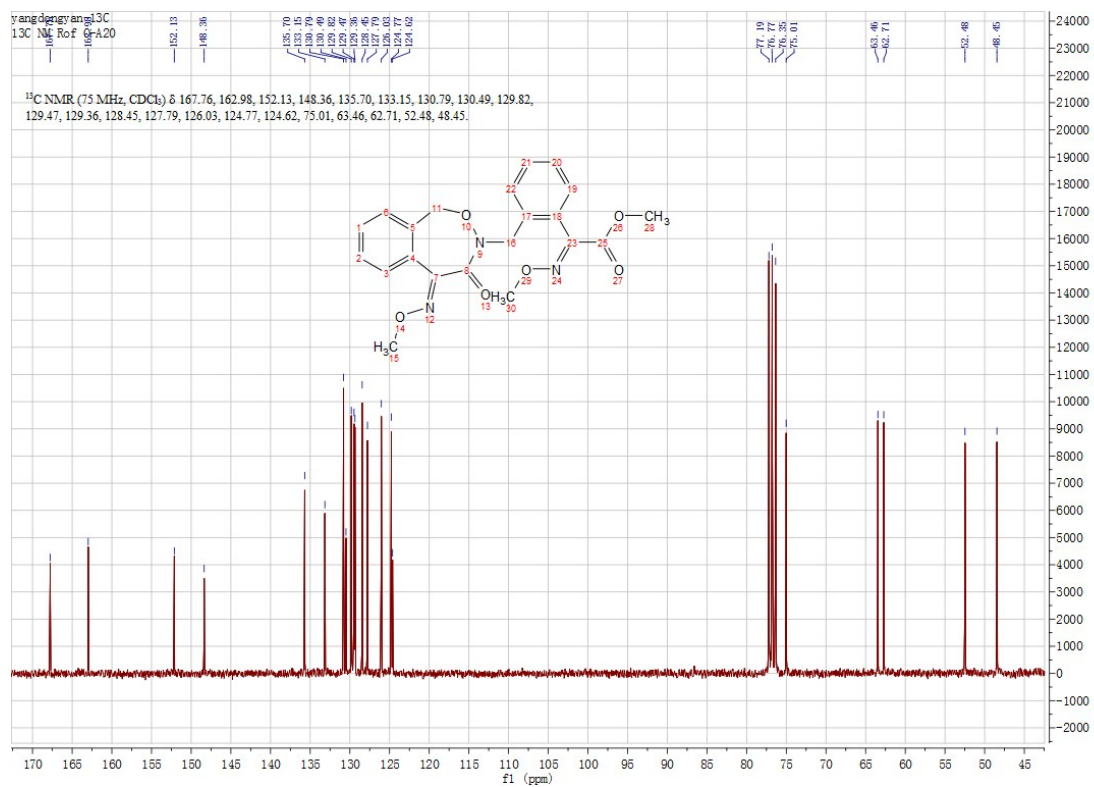
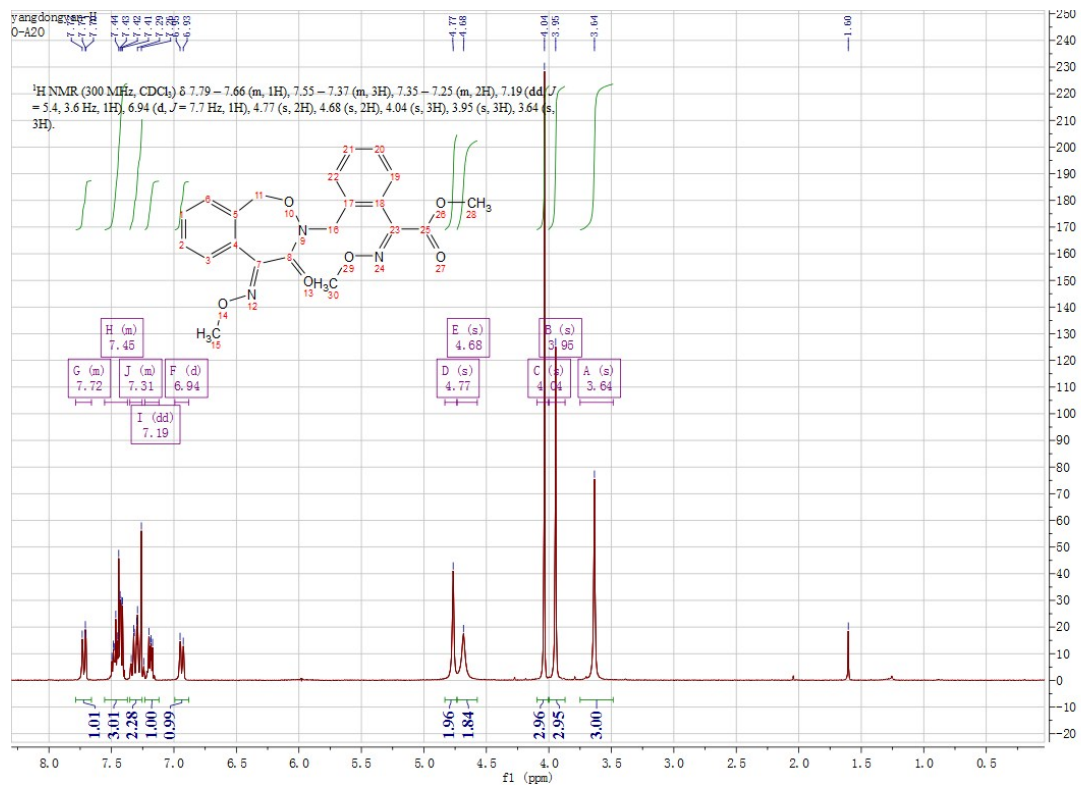


Data for (E)-3-((6-chloropyridin-3-yl)methyl)-5-(methoxyimino)-3,5-dihydrobenzo[e][1,2]oxazepin-4(1H)-one (**5-14**): yield 68 %; yellowish solid; mp 109-111 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.45 (d,  $J = 2.4$  Hz, 1H), 7.84 – 7.71 (m, 2H), 7.46 – 7.31 (m, 3H), 7.07 (d,  $J = 7.3$  Hz, 1H), 5.09 (s, 2H), 4.84 (s, 2H), 4.07 (s, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  168.01, 151.67, 151.10, 149.71, 139.17, 134.82, 130.93, 129.79, 129.41, 126.43, 124.66, 124.56, 124.14, 74.84, 62.84, 46.73. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{16}\text{H}_{15}\text{ClN}_3\text{O}_3$  ( $\text{M}+\text{H}$ ) $^+$  332.0796, found 332.0792.

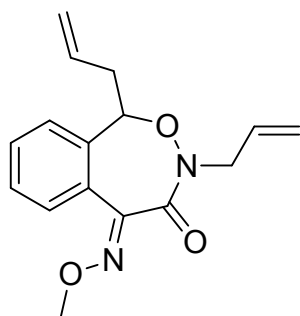
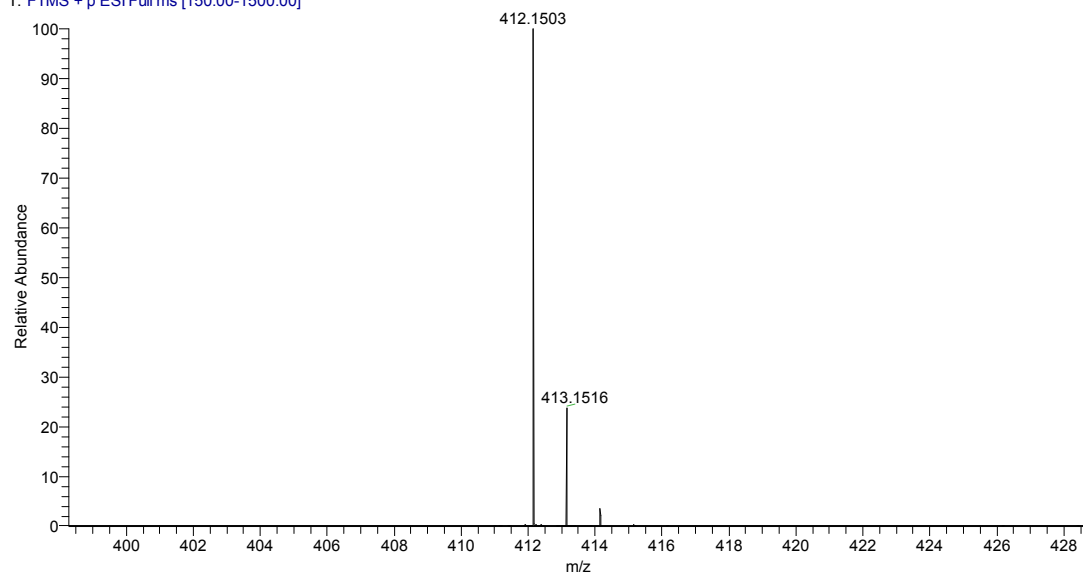




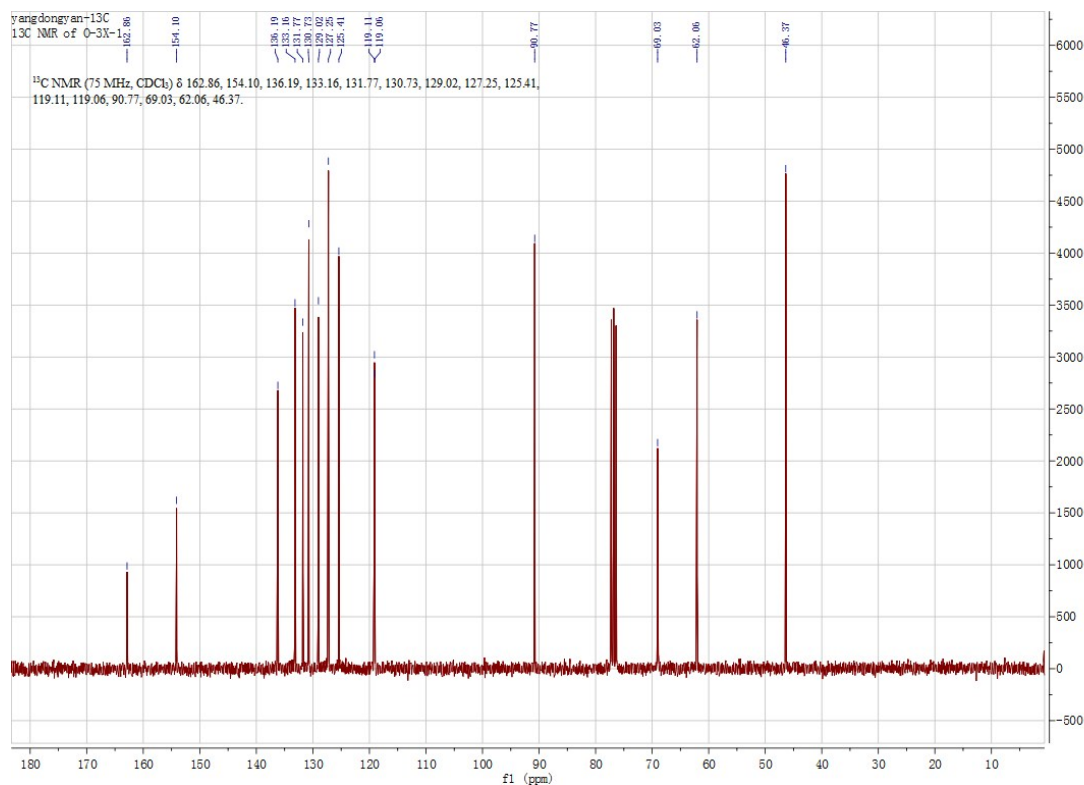
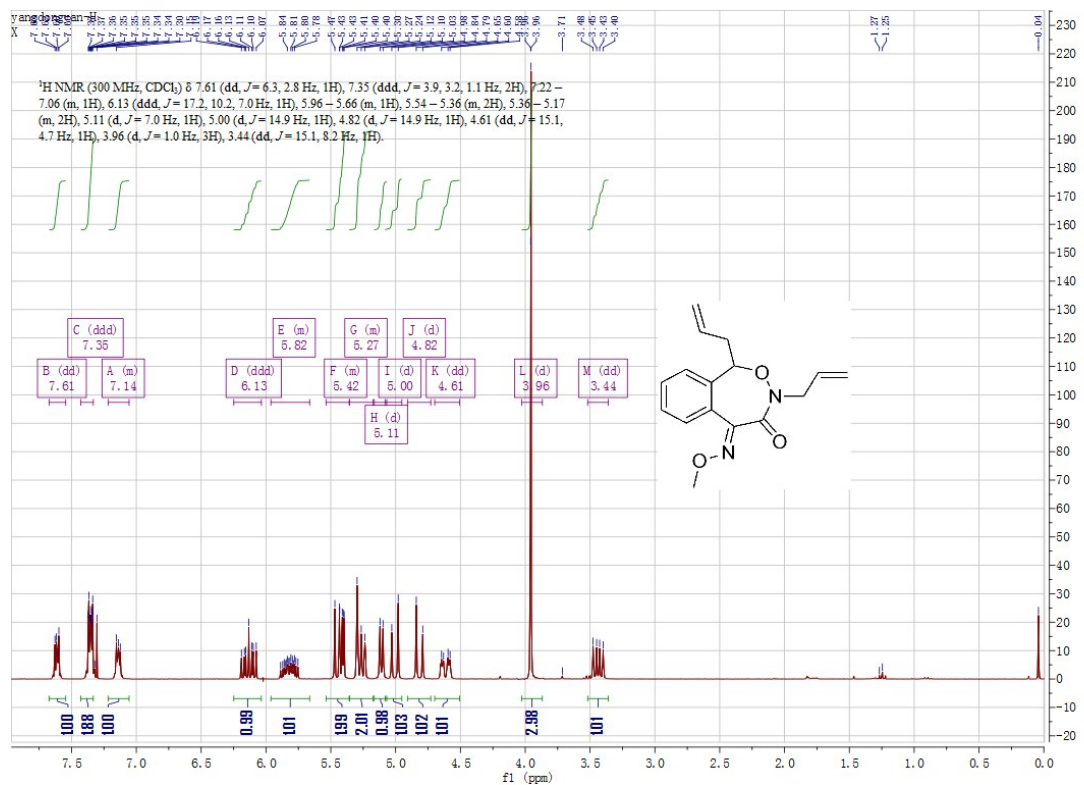
*Data for (E)-methyl 2-(methoxyimino)-2-(2-(((E)-5-(methoxyimino)-4-oxo-4,5-dihydrobenzo[e][1,2]oxazepin-3(1H)-yl)methyl)phenyl)acetate (5-15):* yield 63 %; white solid; mp 147 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.79 – 7.66 (m, 1H), 7.55 – 7.37 (m, 3H), 7.35 – 7.25 (m, 2H), 7.19 (dd, *J* = 5.4, 3.6 Hz, 1H), 6.94 (d, *J* = 7.7 Hz, 1H), 4.77 (s, 2H), 4.68 (s, 2H), 4.04 (s, 3H), 3.95 (s, 3H), 3.64 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 167.76, 162.98, 152.13, 148.36, 135.70, 133.15, 130.79, 130.49, 129.82, 129.47, 129.36, 128.45, 127.79, 126.03, 124.77, 124.62, 75.01, 63.46, 62.71, 52.48, 48.45. HRMS (ESI) *m/z* calcd for C<sub>21</sub>H<sub>21</sub>N<sub>3</sub>O<sub>6</sub> (M+H)<sup>+</sup> 412.1503, found 412.1503.



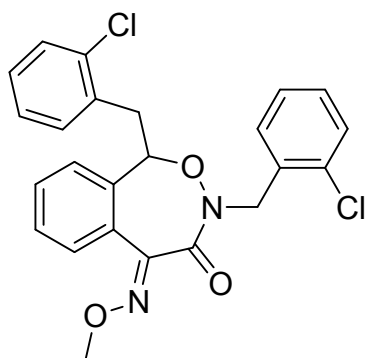
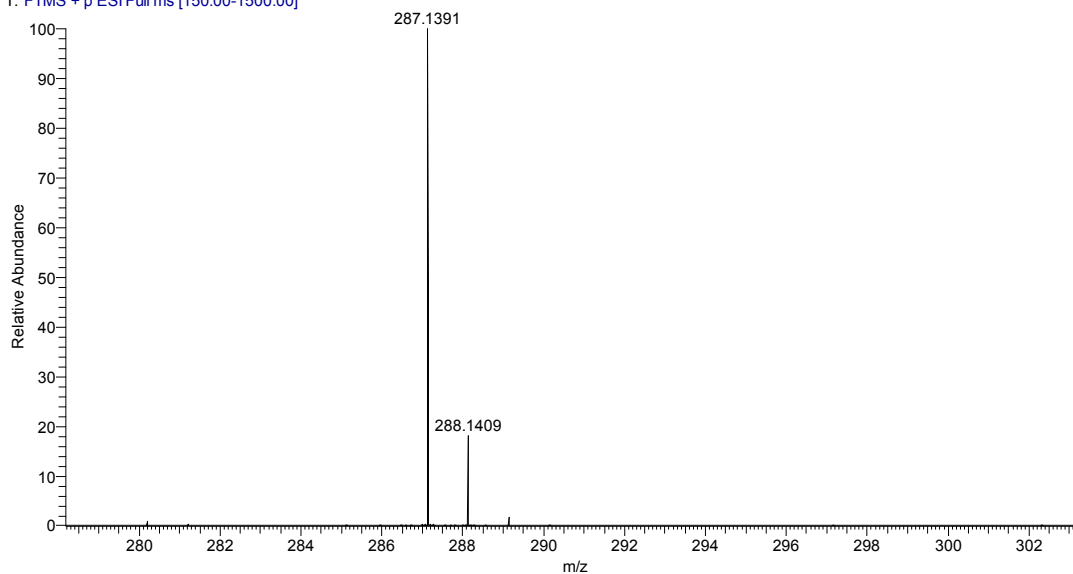
2\_160522114352 #68 RT: 0.72 AV: 1 NL: 6.17E9  
T: FTMS + p ESI Full ms [150.00-1500.00]



Data for (E)-1,3-diallyl-5-(methoxyimino)-3,5-dihydrobenzo[e][1,2]oxazepin-4(1H)-one (**5-16**): yield 42%; white solid; mp 52 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.61 (dd,  $J = 6.3, 2.8$  Hz, 1H), 7.35 (ddd,  $J = 3.9, 3.2, 1.1$  Hz, 2H), 7.22 – 7.06 (m, 1H), 6.13 (ddd,  $J = 17.2, 10.2, 7.0$  Hz, 1H), 5.96 – 5.66 (m, 1H), 5.54 – 5.36 (m, 2H), 5.36 – 5.17 (m, 2H), 5.11 (d,  $J = 7.0$  Hz, 1H), 5.00 (d,  $J = 14.9$  Hz, 1H), 4.82 (d,  $J = 14.9$  Hz, 1H), 4.61 (dd,  $J = 15.1, 4.7$  Hz, 1H), 3.96 (d,  $J = 1.0$  Hz, 3H), 3.44 (dd,  $J = 15.1, 8.2$  Hz, 1H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  162.86, 154.10, 136.19, 133.16, 131.77, 130.73, 129.02, 127.25, 125.41, 119.11, 119.06, 90.77, 69.03, 62.06, 46.37. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{16}\text{H}_{18}\text{N}_2\text{O}_3$  ( $\text{M}+\text{H}$ ) $^+$  287.1390, found 287.1391.

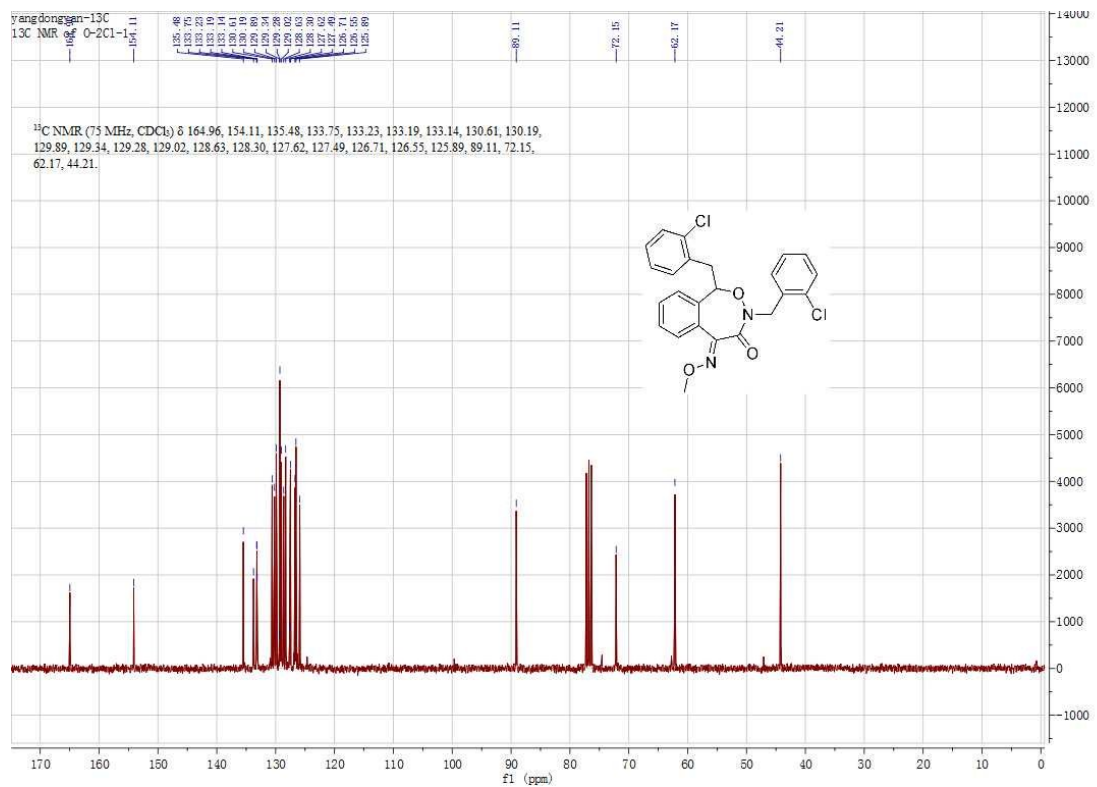
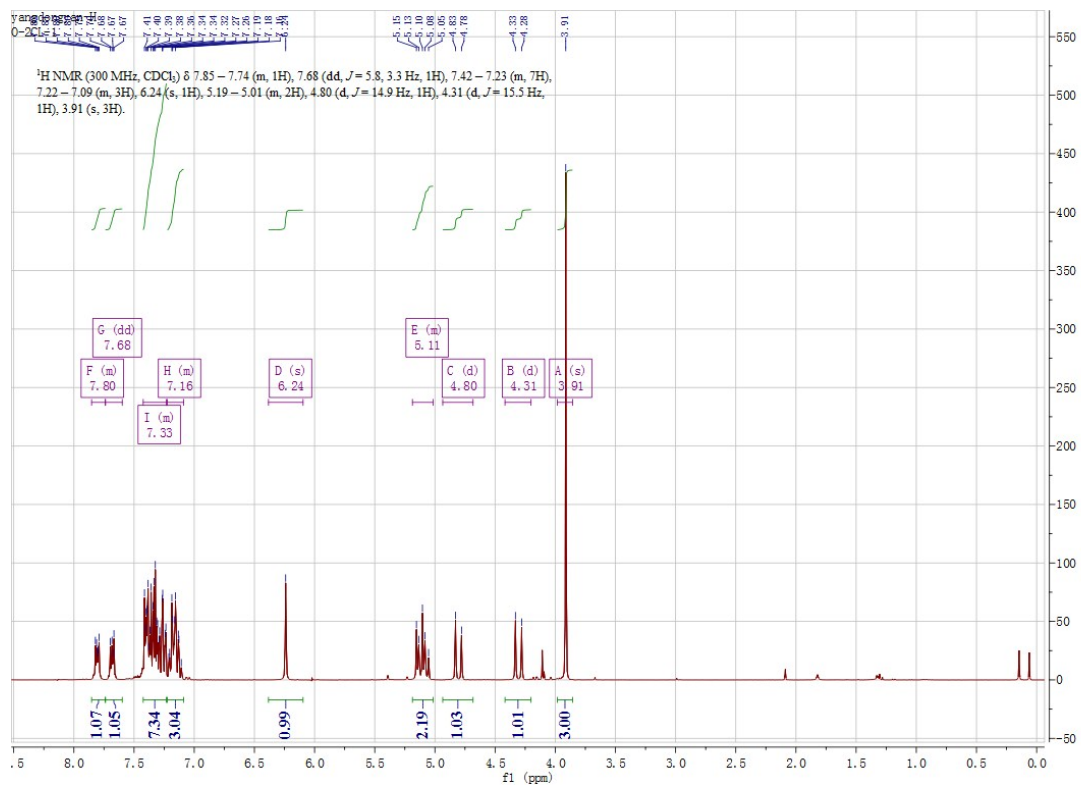


16 #66 RT: 0.70 AV: 1 NL: 1.04E10  
T: FTMS + p ESI Full ms [150.00-1500.00]

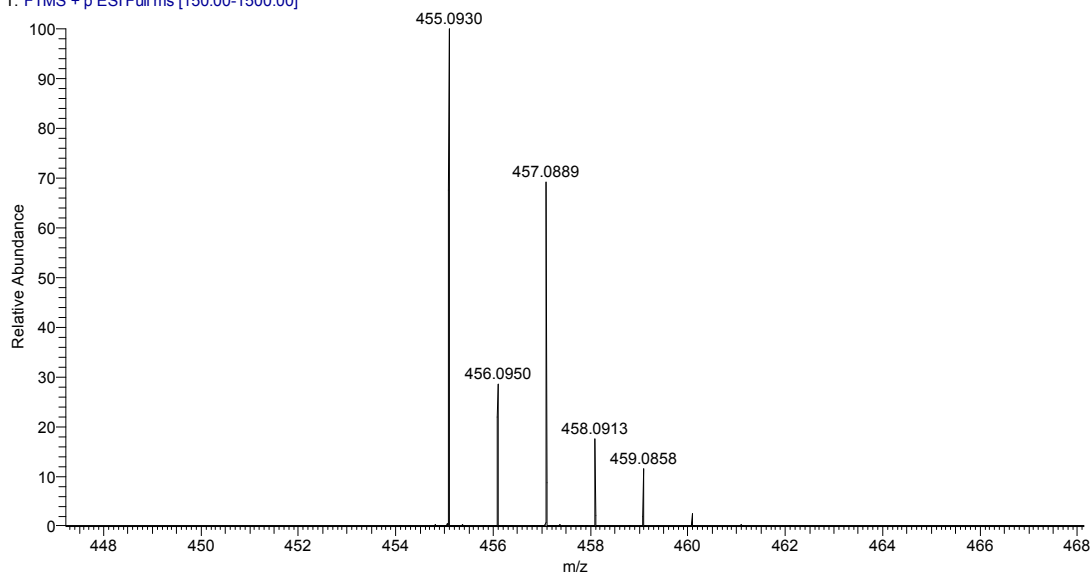


Data for (E)-1,3-bis(2-chlorobenzyl)-5-(methoxyimino)-3,5-dihydrobenzo[e][1,2]oxazepin-4(1H)-one (**5-17**): yield 54 %; white solid; mp 96-97 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 – 7.74 (m, 1H), 7.68 (dd,  $J = 5.8, 3.3$  Hz, 1H), 7.42 – 7.23 (m, 7H), 7.22 – 7.09 (m, 3H), 6.24 (s, 1H), 5.19 – 5.01 (m, 2H), 4.80 (d,  $J = 14.9$  Hz, 1H), 4.31 (d,  $J = 15.5$  Hz, 1H), 3.91 (s, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  164.96, 154.11, 135.48, 133.75, 133.23, 133.19, 133.14, 130.61, 130.19, 129.89, 129.34, 129.28, 129.02, 128.63, 128.30, 127.62, 127.49, 126.71, 126.55, 125.89, 89.11, 72.15, 62.17, 44.21. . HRMS (ESI)  $m/z$  calcd for  $\text{C}_{24}\text{H}_{20}\text{Cl}_2\text{N}_2\text{O}_3$  ( $\text{M}+\text{H}$ ) $^+$  455.0924, found 455.0930.

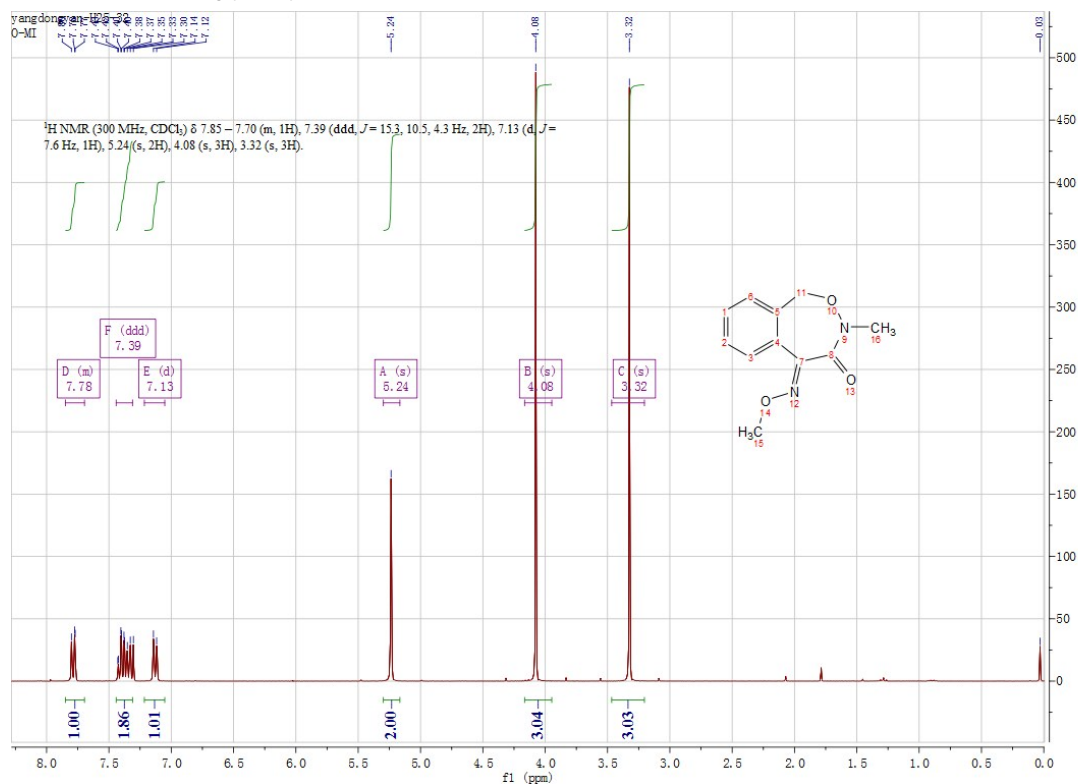


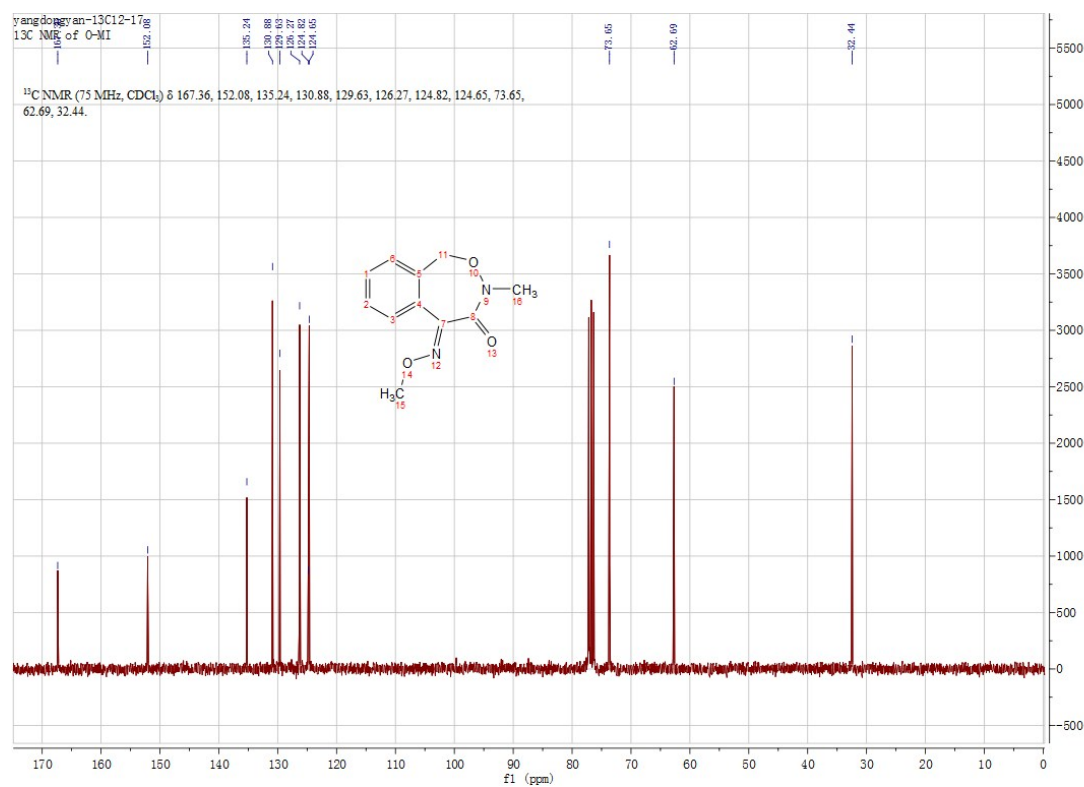


17 #312 RT: 3.38 AV: 1 NL: 3.58E9  
T: FTMS + p ESI Full ms [150.00-1500.00]

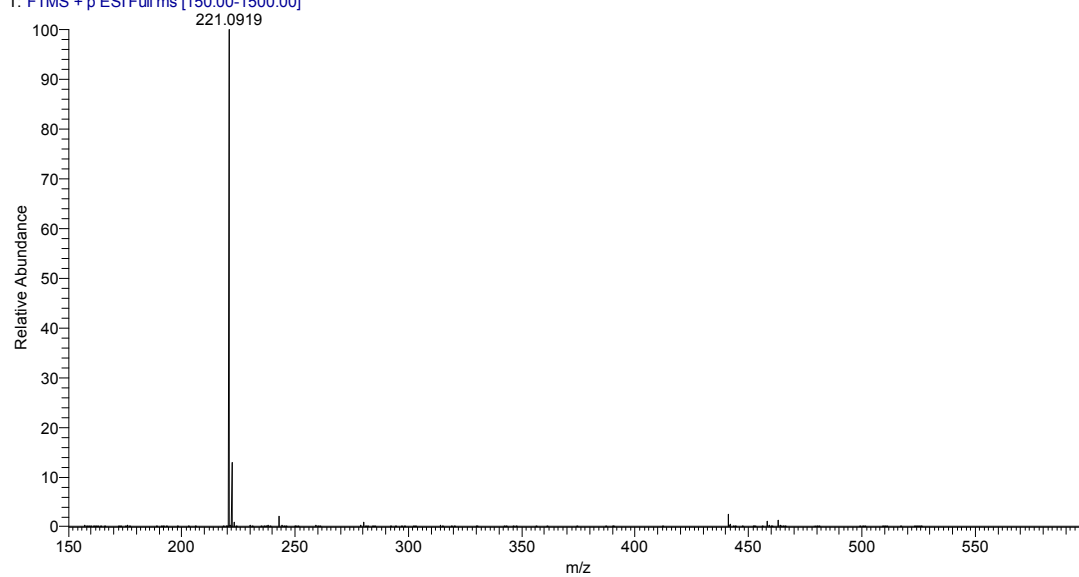


Data for (E)-5-(methoxyimino)-3-methyl-3,5-dihydrobenzo[e][1,2]oxazepin-4(1H)-one (**5-18**): yield 83 %; white solid; mp 106-107 °C;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 – 7.70 (m, 1H), 7.39 (ddd,  $J = 15.3, 10.5, 4.3$  Hz, 2H), 7.13 (d,  $J = 7.6$  Hz, 1H), 5.24 (s, 2H), 4.08 (s, 3H), 3.32 (s, 3H).  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  167.36, 152.08, 135.24, 130.88, 129.63, 126.27, 124.82, 124.65, 73.65, 62.69, 32.44. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{11}\text{H}_{12}\text{N}_2\text{O}_3$  (M+H) $^+$  221.0921, found 221.0919.

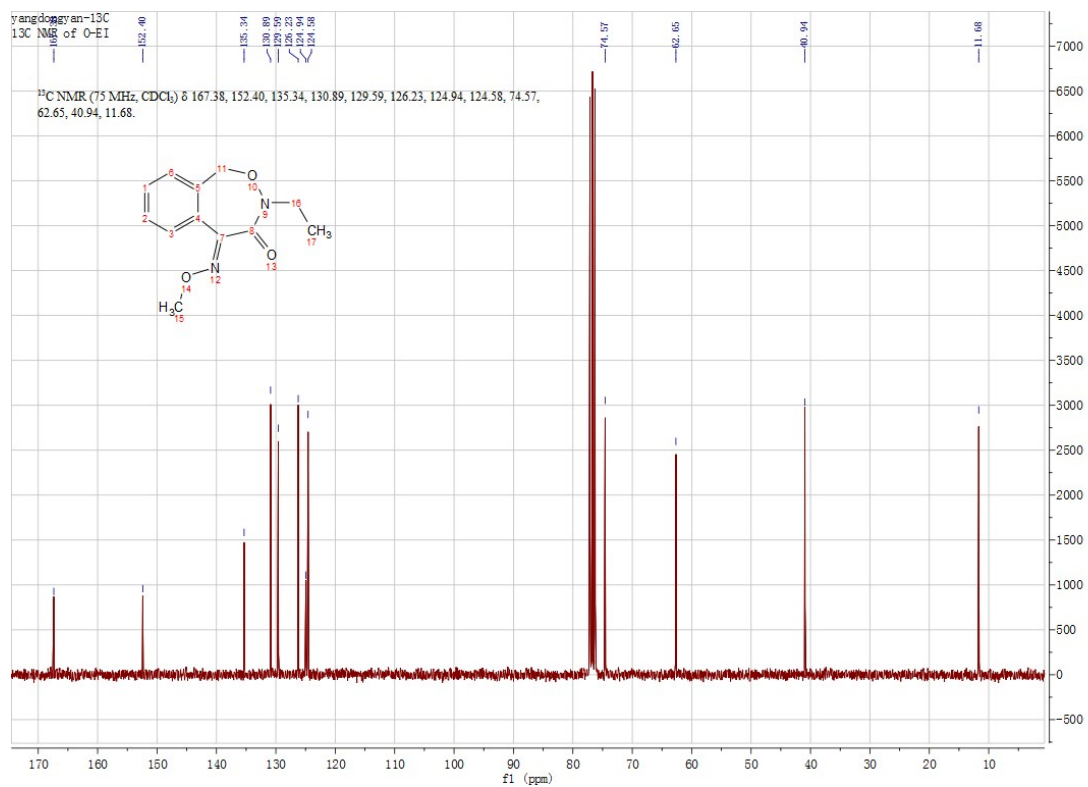
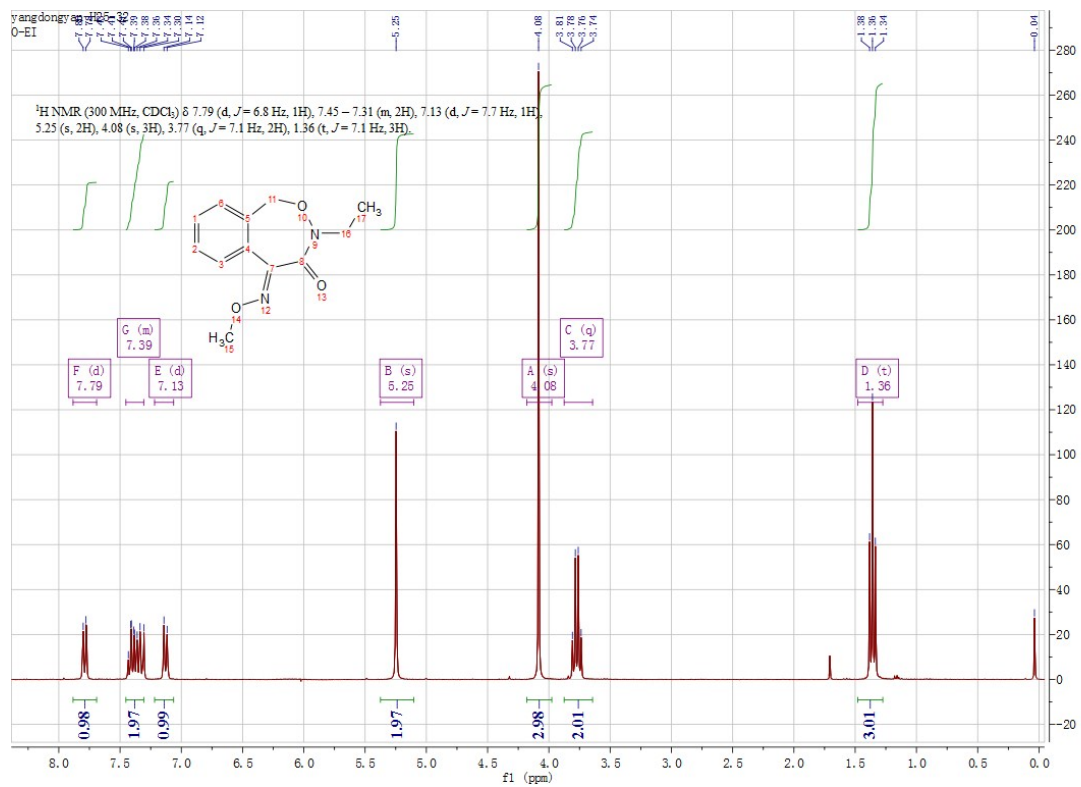




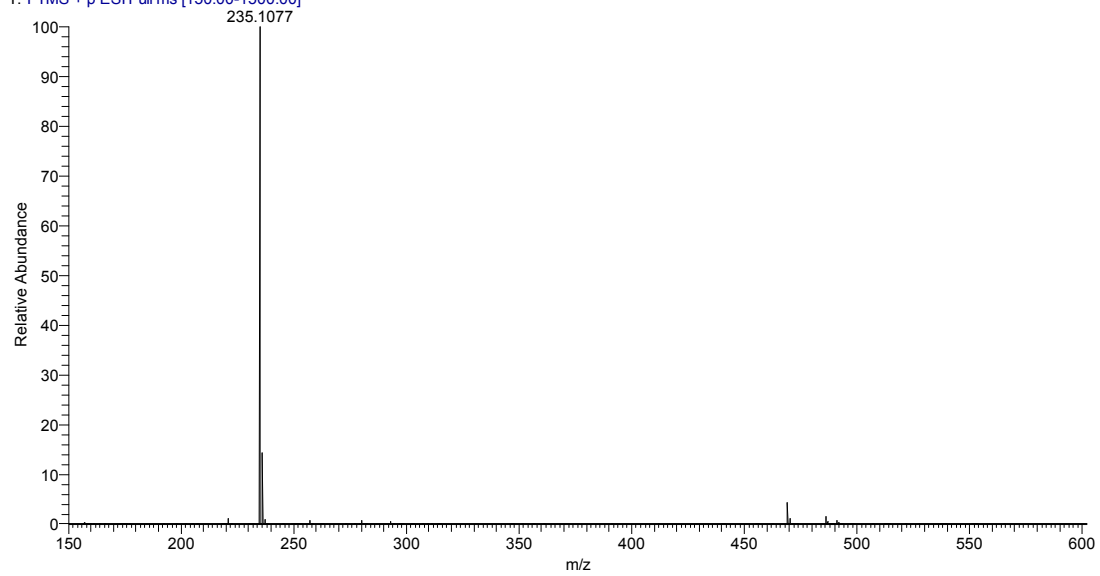
5 #60 RT: 0.64 AV: 1 NL: 1.74E10  
 T: FTMS + p ESI Full ms [150.00-1500.00]



Data for (E)-3-ethyl-5-(methoxyimino)-3,5-dihydrobenzo[e][1,2]oxazepin-4(1H)-one (**5-19**):  
 yield 63 %; white solid; mp 61-62 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.79 (d, J = 6.8 Hz, 1H), 7.45 - 7.31 (m, 2H), 7.13 (d, J = 7.7 Hz, 1H), 5.25 (s, 2H), 4.08 (s, 3H), 3.77 (q, J = 7.1 Hz, 2H), 1.36 (t, J = 7.1 Hz, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 167.38, 152.40, 135.34, 130.89, 129.59, 126.23, 124.94, 124.58, 74.57, 62.65, 40.94, 11.68. HRMS (ESI) m/z calcd for C<sub>12</sub>H<sub>14</sub>N<sub>2</sub>O<sub>3</sub> (M+H)<sup>+</sup> 235.1070, found 235.1070.



6 #68 RT: 0.72 AV: 1 NL: 1.72E10  
T: FTMS + p ESI Full ms [150.00-1500.00]



## Single crystal X-Ray data for compound 5-09

**Table 1:** Crystal data and structure refinement for (5-09)

Identification code	(5-09)
Empirical formula	C <sub>17</sub> H <sub>15</sub> ClN <sub>2</sub> O <sub>3</sub>
Formula weight	330.76
Temperature / K	104.8
Crystal system	orthorhombic
Space group	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
a / Å, b / Å, c / Å	8.7758(3), 10.3761(4), 12.7000(2)
α / °, β / °, γ / °	90.00, 90.00, 90.00
Volume / Å <sup>3</sup>	1529.75(10)
Z	4
ρ <sub>calc</sub> / mg mm <sup>-3</sup>	1.436
μ / mm <sup>-1</sup>	0.267
F(000)	688
Crystal size / mm <sup>3</sup>	0.30 × 0.25 × 0.24
2θ range for data collection	6.54 to 52°
Index ranges	-10 ≤ h ≤ 10, -12 ≤ k ≤ 10, -11 ≤ l ≤ 11
Reflections collected	6446
Independent reflections	3009 [R(int) = 0.0255 (inf-0.9Å)]
Data/restraints/parameters	3009/0/209
Goodness-of-fit on F <sup>2</sup>	1.043

Final R indexes [ $I > 2\sigma(I)$ i.e. $\sigma(I) > 2\sigma(I)$ ]	$R_1 = 0.0306$ , $wR_2 = 0.0655$
Final R indexes [all data]	$R_1 = 0.0337$ , $wR_2 = 0.0675$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.174/-0.195
Flack Parameters	0.00(5)
Completeness	0.997

Table 2 Fractional Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for (5-09).  $U_{eq}$  is defined as 1/3 of the trace of the orthogonalised  $U_{IJ}$  tensor.

Atom	$x$	$y$	$z$	$U(eq)$
C11	5466.1(5)	4290.5(5)	345.5(3)	21.05(12)
O3	7387.5(14)	-1527.3(12)	-3836.8(7)	16.5(3)
N2	7990.7(15)	-555.3(16)	-3347.5(8)	15.2(3)
O1	6722.2(13)	2584.6(13)	-3564.9(7)	16.3(3)
O2	10112.4(13)	1370.5(13)	-2817.3(7)	18.6(3)
C3	8096.8(17)	712.9(18)	-4606.2(10)	13.4(4)
C14	6369.0(18)	4144.0(19)	-578.5(10)	15.3(4)
N1	8242.5(16)	2664.9(16)	-3285.7(9)	15.7(3)
C4	7411.2(19)	1835.4(19)	-4908.6(10)	14.8(4)
C5	6687(2)	2861.9(19)	-4400.0(11)	17.0(4)

C12	6565 (2)	4747.5 (18)	-1943.7 (10)	16.0 (4)
C6	8677.5 (19)	-201.0 (19)	-5137.5 (10)	16.0 (4)
C2	8278.8 (18)	479.3 (18)	-3732.7 (10)	13.3 (4)
C9	7304 (2)	1991 (2)	-5732.8 (11)	19.6 (4)
C10	8602.6 (19)	3826.0 (17)	-2837.1 (10)	15.5 (4)
C8	7847 (2)	1061 (2)	-6251.1 (11)	21.4 (4)
C15	7575 (2)	3298.8 (19)	-663.0 (11)	17.4 (4)
C11	7790.9 (19)	3918.6 (17)	-2044.7 (10)	13.4 (4)
C1	8962.3 (19)	1521.5 (18)	-3214.5 (10)	13.8 (4)
C17	6885 (2)	-2564.8 (19)	-3338.3 (11)	19.2 (4)
C7	8545 (2)	-39 (2)	-5951.3 (11)	20.0 (4)
C13	5849 (2)	4878.6 (19)	-1210.8 (11)	18.1 (4)
C16	8285 (2)	3192.8 (19)	-1399.0 (11)	17.6 (4)



Table 3 Anisotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for (5-09).  
 The Anisotropic displacement factor exponent takes the form:  $-2\pi^2 [h^2 a^2 U_{11} + \dots + 2hka \times b \times U_{12}]$

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
C11	20.8 (2)	26.6 (3)	15.8 (2)	-1.4 (2)	4.16 (18)	-1.4 (2)
O3	24.0 (6)	10.6 (7)	14.9 (6)	-1.3 (5)	-2.8 (5)	-4.9 (6)
N2	17.3 (7)	13.0 (9)	15.4 (7)	-3.4 (7)	-1.4 (6)	0.5 (7)
O1	12.2 (5)	20.5 (8)	16.1 (6)	-0.5 (6)	-1.3 (5)	0.5 (6)
O2	19.4 (6)	17.7 (7)	18.6 (6)	-1.1 (6)	-7.1 (5)	1.3 (5)
C3	12.3 (7)	14.0 (9)	14.0 (8)	1.1 (8)	-1.3 (7)	-2.8 (7)
C14	15.4 (8)	16.4 (10)	13.9 (8)	-2.5 (8)	1.8 (7)	-5.8 (8)
N1	12.4 (7)	17.3 (9)	17.4 (8)	-3.6 (7)	-3.2 (6)	0.7 (6)
C4	11.7 (8)	17.3 (10)	15.5 (9)	0.8 (8)	-1.2 (7)	-4.1 (8)
C5	17.7 (8)	15.2 (10)	18.2 (9)	2.7 (8)	-6.0 (8)	1.3 (8)
C12	17.0 (8)	14.9 (10)	16.2 (9)	3.1 (8)	-1.6 (8)	-0.8 (8)
C6	14.9 (8)	15.9 (10)	17.3 (9)	-0.7 (8)	0.8 (7)	-1.9 (8)
C2	10.6 (7)	15.5 (11)	13.9 (8)	0.0 (7)	0.1 (7)	0.7 (7)
C9	18.4 (9)	21.6 (11)	18.7 (10)	7.1 (9)	-3.0 (8)	-4.0 (8)
C10	19.3 (9)	12.1 (10)	14.9 (9)	-1.2 (7)	-0.2 (7)	-1.9 (8)
C8	21.0 (9)	30.8 (12)	12.4 (9)	2.5 (8)	-0.9 (7)	-7.3 (8)

C15	21.5 (9)	15.3 (10)	15.6 (9)	1.5 (8)	-2.9 (8)	-1.0 (8)
C11	16.2 (8)	10.4 (9)	13.6 (9)	-2.6 (7)	-0.7 (7)	-3.9 (7)
C1	15.9 (8)	15.3 (10)	10.2 (8)	1.5 (7)	3.1 (7)	-1.4 (7)
C17	25.4 (10)	14.1 (10)	18.1 (10)	0.5 (8)	-0.7 (8)	-5.2 (8)
C7	18.9 (9)	25.8 (12)	15.2 (9)	-3.6 (8)	1.7 (8)	-5.4 (9)
C13	16.1 (8)	16.6 (10)	21.7 (10)	-1.4 (8)	1.4 (8)	-0.7 (8)
C16	19.6 (8)	13.7 (10)	19.5 (10)	-0.3 (8)	-0.1 (8)	4.9 (8)

Table 4 Bond Lengths for (5-09).

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C11	C14	1.7494 (17)	N1	C1	1.349 (2)
O3	N2	1.4048 (19)	C4	C5	1.506 (3)
O3	C17	1.434 (2)	C4	C9	1.397 (2)
N2	C2	1.279 (2)	C12	C11	1.388 (2)
O1	N1	1.4167 (17)	C12	C13	1.389 (3)
O1	C5	1.432 (2)	C6	C7	1.382 (2)
O2	C1	1.220 (2)	C2	C1	1.512 (2)
C3	C4	1.406 (3)	C9	C8	1.384 (3)
C3	C6	1.398 (2)	C10	C11	1.513 (2)
C3	C2	1.496 (2)	C8	C7	1.390 (3)
C14	C15	1.382 (3)	C15	C16	1.389 (3)
C14	C13	1.385 (3)	C11	C16	1.390 (2)
N1	C10	1.456 (2)			

Table 5 Bond Angles for (5-09).

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N2	O3	C17	108.25(12)	C7	C6	C3	121.22(18)
C2	N2	O3	112.40(13)	N2	C2	C3	127.69(16)
N1	O1	C5	109.43(12)	N2	C2	C1	112.79(15)
C4	C3	C2	122.30(16)	C3	C2	C1	119.42(15)
C6	C3	C4	119.15(16)	C8	C9	C4	121.33(19)
C6	C3	C2	118.52(16)	N1	C10	C11	113.95(14)
C15	C14	C11	119.56(14)	C9	C8	C7	119.74(17)
C15	C14	C13	121.52(16)	C14	C15	C16	119.03(17)
C13	C14	C11	118.92(14)	C12	C11	C10	120.79(16)
O1	N1	C10	115.12(14)	C12	C11	C16	118.82(16)
C1	N1	O1	114.74(14)	C16	C11	C10	120.37(16)
C1	N1	C10	125.45(14)	O2	C1	N1	123.28(17)
C3	C4	C5	124.16(16)	O2	C1	C2	123.44(17)
C9	C4	C3	118.84(18)	N1	C1	C2	113.07(15)

C9	C4	C5	116.89(17)	C6	C7	C8	119.68(18)
01	C5	C4	113.86(15)	C14	C13	C12	118.50(17)
C11	C12	C13	121.31(17)	C15	C16	C11	120.80(17)

Table 6 Torsion Angles for (5-09).

<b>A</b>	<b>B</b>	<b>C</b>	<b>D</b>	<b>Angle/°</b>
C11	C14	C15	C16	-179.86(14)
C11	C14	C13	C12	-179.46(14)
03	N2	C2	C3	-2.4(2)
03	N2	C2	C1	-178.69(13)
N2	C2	C1	O2	55.6(2)
N2	C2	C1	N1	-129.43(16)
01	N1	C10	C11	67.20(19)
01	N1	C1	O2	-162.21(14)
01	N1	C1	C2	22.8(2)
C3	C4	C5	O1	-1.4(2)
C3	C4	C9	C8	0.4(3)
C3	C6	C7	C8	1.2(3)
C3	C2	C1	O2	-121.05(19)

C3	C2	C1	N1	53.9 (2)
C14	C15	C16	C11	-0.3 (3)
N1	01	C5	C4	69.47 (19)
N1	C10	C11	C12	-104.76 (19)
N1	C10	C11	C16	76.7 (2)
C4	C3	C6	C7	-2.1 (2)
C4	C3	C2	N2	134.29 (19)
C4	C3	C2	C1	-49.6 (2)
C4	C9	C8	C7	-1.4 (3)
C5	01	N1	C10	103.84 (16)
C5	01	N1	C1	-99.02 (17)
C5	C4	C9	C8	-175.91 (16)
C12	C11	C16	C15	-0.5 (3)
C6	C3	C4	C5	177.34 (16)
C6	C3	C4	C9	1.3 (2)
C6	C3	C2	N2	-47.9 (2)
C6	C3	C2	C1	128.19 (17)
C2	C3	C4	C5	-4.9 (3)
C2	C3	C4	C9	179.08 (16)
C2	C3	C6	C7	-179.97 (16)
C9	C4	C5	01	174.77 (15)
C9	C8	C7	C6	0.6 (3)
C10	N1	C1	02	-7.8 (3)

C10	N1	C1	C2	177.22 (15)
C10	C11	C16	C15	178.13 (17)
C15	C14	C13	C12	0.3 (3)
C11	C12	C13	C14	-1.1 (3)
C1	N1	C10	C11	-87.1 (2)
C17	O3	N2	C2	-171.16 (15)
C13	C14	C15	C16	0.4 (3)
C13	C12	C11	C10	-177.42 (16)
C13	C12	C11	C16	1.2 (3)

Table 7 Hydrogen Atom Coordinates ( $\text{\AA} \times 10^4$ ) and Isotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for (5-09).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)
H5A	7220	3689	-4495	20
H5B	5613	2972	-4567	20
H12	6208	5235	-2385	19
H6	9172	-947	-4935	19
H9	6848	2749	-5942	23
H10A	8330	4587	-3163	19
H10B	9716	3854	-2743	19

H8	7744	1175	-6810	26
H15	7913	2797	-224	21
H17A	6576	-3296	-3671	29
H17B	6016	-2278	-3017	29
H17C	7718	-2829	-2986	29
H7	8929	-677	-6304	24
H13	5022	5459	-1145	22
H16	9118	2617	-1462	21

## Experimental

Single crystals of  $C_{17}H_{15}ClN_2O_3$  [(5-09)] were recrystallised from [dichloromethane/n-hexane] mounted in inert oil and transferred to the cold gas stream of the diffractometer.

### Crystal structure determination of [(5-09)]

**Crystal Data.**  $C_{17}H_{15}ClN_2O_3$ ,  $M=330.76$ , orthorhombic,  $a = 8.7758(3) \text{ \AA}$ ,  $b = 10.3761(4) \text{ \AA}$ ,  $c = 16.7996(6) \text{ \AA}$ ,  $U = 1529.75(10) \text{ \AA}^3$ ,  $T = 104.8$ , space group  $P2_12_12_1$  (no. 19),  $Z = 4$ ,  $\mu(\text{Mo K}\alpha) = 0.267$ , 6446 reflections measured, 3009 unique ( $R_{\text{int}} = 0.0255$ ) which were used in all calculations. The final  $wR(F_2)$  was 0.0675 (all data).