

**Supplementary Information**

**for**

**Medium-ring benzolactams via nickel-catalyzed denitrogenative re-cyclization of  
benzotriazinones with di(pseudo)haloalkanes**

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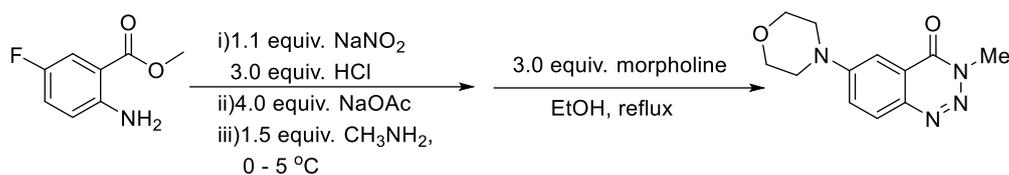
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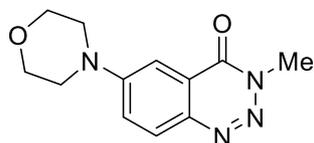
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## Preparation of new compound 1r



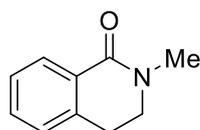
To a 250 mL round-bottom flask was added methyl 2-amino-5-fluorobenzoate (8.450 g, 50 mmol, 1.0 equiv.) in  $\text{HCl}$  (con., 12.5 mL, 150 mmol) followed by solution of  $\text{NaNO}_2$  (3.795 g, 55 mmol, 1.1 equiv.) in water (10 mL) at  $0^\circ\text{C}$ . The resulting solution was stirred for 1 h. Then, a solution of  $\text{NaOAc}$  (16.405 g, 200 mmol, 4.0 equiv.) in water (50 mL) was slowly added and followed by addition of methanamine (2.325 g, 75 mmol, 1.5 equiv.) at  $0^\circ\text{C}$ . The resulting mixture was stirred at  $0^\circ\text{C}$  for 6 h. The precipitate was collected by filtration, washed with water (100 mL), and purified by recrystallization from ethanol to afford triazenes. The above triazene was refluxed in ethanol (100 mL) with excess morpholine (13.070 g, 150 mmol, 3.0 equiv.) until triazene was completely consumed (TLC). The reaction mixture was cooled to room temperature to afford N-alkyl benzotriazinone as crystals.<sup>[1]</sup>

## Characterization data for benzotriazinones 1r



3-Methyl-6-morpholinobenzo[d][1,2,3]triazin-4(3H)-one (**1r**) White powders (8.6 g, 70%), m.p. =  $187 - 188^\circ\text{C}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ (ppm): 7.97 (d,  $J = 9.2$  Hz, 1H), 7.50 (d,  $J = 2.8$  Hz, 1H), 7.40 (dd,  $J = 9.2, 2.8$  Hz, 1H), 3.98 (s, 3H), 3.87 – 3.85 (m, 4H), 3.41 – 3.38 (m, 4H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ (ppm): 156.2, 153.1, 137.9, 129.7, 121.3, 121.2, 105.1, 66.3, 47.4, 37.1. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{12}\text{H}_{15}\text{N}_4\text{O}_2$  247.1195, found 247.1201.

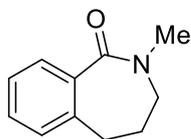
## Characterization data for six-membered ring benzolactams 8aa



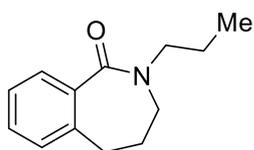
2-Methyl-3,4-dihydroisoquinolin-1(2H)-one (**8aa**)<sup>[2]</sup> Colorless oil (32 mg, 20%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ (ppm): 8.06 – 8.04 (m, 1H), 7.39 – 7.35 (m, 1H), 7.31 – 7.28 (m, 1H), 7.03 (d,  $J = 7.6$  Hz,

1H), 3.53 (t,  $J = 6.4$  Hz, 2H), 3.12 (s, 3H), 2.97 (t,  $J = 6.4$  Hz, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ (ppm): 164.8, 138.0, 131.5, 129.4, 128.1, 127.0, 126.9, 48.1, 35.2, 27.9.

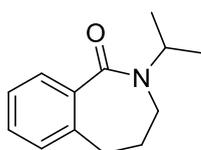
### Characterization data for tetrahydrobenzoazepin-1-ones



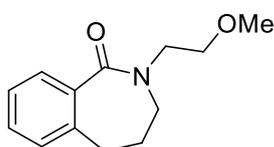
N-Methyltetrahydrobenzoazepin-1-one (**9aa**)<sup>[3]</sup> White powders (172 mg, 98%; 161 mg, 92% from **4b**; 150 mg, 86% from **4c**), m.p. = 53 – 54 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ (ppm): 7.63 (dd,  $J = 7.2$ , 1.2 Hz, 1H), 7.34 – 7.26 (m, 2H), 7.10 (d,  $J = 7.2$  Hz, 1H), 3.20 – 3.15 (m (overlapped), 5H), 2.74 (t,  $J = 7.2$  Hz, 2H), 2.05 – 1.99 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ (ppm): 171.2, 137.2, 136.2, 130.6, 128.3, 128.2, 126.8, 47.9, 34.4, 30.0, 28.7.



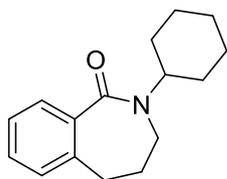
N-Propyltetrahydrobenzoazepin-1-one (**9ba**) White powders (187 mg, 92%), m.p. = 65 – 66 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ (ppm): 7.66 – 7.64 (m, 1H), 7.35 – 7.27 (m, 2H), 7.12 – 7.10 (m, 1H), 3.52 (t,  $J = 7.6$  Hz, 2H), 3.18 (t,  $J = 6.4$  Hz, 2H), 2.77 (t,  $J = 7.2$  Hz, 2H), 2.04 – 1.97 (m, 2H), 1.71 – 1.62 (m, 2H), 0.97 (t,  $J = 7.2$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ (ppm): 171.0, 137.3, 136.7, 130.7, 128.6, 128.2, 127.0, 49.1, 46.3, 30.3, 30.1, 22.3, 11.6. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{13}\text{H}_{18}\text{NO}$  204.1388, found 204.1387.



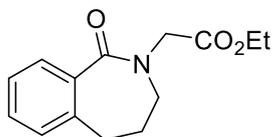
N-Isopropyltetrahydrobenzoazepin-1-one (**9ca**)<sup>[4]</sup> White powders (177 mg, 87%), m.p. = 84 – 85 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ (ppm): 7.67 – 7.65 (m, 1H), 7.36 – 7.27 (m, 2H), 7.11 (d,  $J = 7.2$  Hz, 1H), 5.05 – 4.94 (m, 1H), 3.09 (t,  $J = 6.8$  Hz, 2H), 2.76 (t,  $J = 7.2$  Hz, 2H), 1.99 – 1.92 (m, 2H), 1.21 (d,  $J = 6.8$  Hz, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ (ppm): 170.7, 137.2, 136.6, 130.6, 128.8, 128.1, 126.9, 44.5, 39.4, 31.4, 30.1, 20.8.



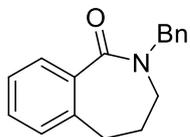
N-(2-Methoxyethyl)tetrahydrobenzoazepin-1-one (**9da**) Colorless oil (172 mg, 90%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ(ppm): 7.62 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.34 – 7.25 (m, 2H), 7.11 – 7.01 (m, 1H), 3.74 (t, *J* = 5.2 Hz, 2H), 3.59 (t, *J* = 5.2 Hz, 2H), 3.35 (s, 3H), 3.23 (t, *J* = 6.4 Hz, 2H), 2.74 (t, *J* = 7.2 Hz, 2H), 2.04 – 1.97 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ(ppm): 171.1, 137.5, 136.1, 130.6, 128.3, 128.1, 126.7, 71.3, 58.6, 47.5, 47.4, 30.1, 29.7. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>13</sub>H<sub>18</sub>NO<sub>2</sub> 220.1338, found 220.1339.



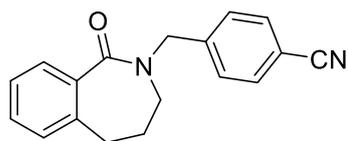
N-Cyclohexyltetrahydrobenzoazepin-1-one (**9ea**) White powders (224 mg, 92%), m.p. = 126 – 127 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ(ppm): 7.66 – 7.64 (m, 1H), 7.35 – 7.27 (m, 2H), 7.10 (d, *J* = 6.8 Hz, 1H), 4.60 – 4.54 (m, 1H), 3.10 (t, *J* = 6.4 Hz, 2H), 2.75 (t, *J* = 7.2 Hz, 2H), 1.96 – 1.89 (m, 2H), 1.82 – 1.80 (m, 4H), 1.70 – 1.66 (m, 1H), 1.50 – 1.34 (m, 4H), 1.16 – 1.06 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ(ppm): 170.7, 137.2, 136.7, 130.5, 128.7, 128.0, 126.8, 52.8, 40.3, 31.4, 31.2, 30.1, 25.7, 25.6. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>16</sub>H<sub>22</sub>NO 244.1701, found 244.1702.



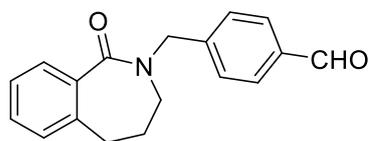
N-(2-Ethoxy-2-oxoethyl)tetrahydrobenzoazepin-1-one (**9fa**) Colorless oil (186 mg, 75%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ(ppm): 7.66 – 7.64 (m, 1H), 7.37 – 7.32 (m, 1H), 7.31 – 7.27 (m, 1H), 7.13 (d, *J* = 7.2 Hz, 1H), 4.31 (s, 2H), 4.20 (q, *J* = 7.2 Hz, 2H), 3.26 (t, *J* = 6.8 Hz, 2H), 2.88 (t, *J* = 6.8 Hz, 2H), 2.08 – 2.01 (m, 2H), 1.27 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ(ppm): 171.6, 169.5, 137.9, 135.3, 131.0, 128.6, 128.3, 126.8, 61.2, 49.5, 47.9, 30.1, 29.4, 14.1. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>14</sub>H<sub>18</sub>NO<sub>3</sub> 248.1287, found 248.1288. IR (KBr): ν(cm<sup>-1</sup>): 1742 (s, C=O), 1635 (s, C=O).



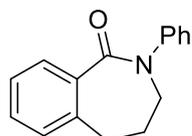
N-Benzyltetrahydrobenzoazepin-1-one (**9ga**)<sup>[5]</sup> Colorless oil (234 mg, 93%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ(ppm): 7.74 – 7.72 (m, 1H), 7.40 – 7.27 (m, 7H), 7.12 – 7.10 (m, 1H), 4.79 (s, 2H), 3.18 (t, *J* = 6.4 Hz, 2H), 2.73 (t, *J* = 7.2 Hz, 2H), 1.81 – 1.74 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ(ppm): 171.1, 138.0, 137.3, 135.9, 130.7, 128.5, 128.2, 127.4, 126.8, 50.2, 45.5, 30.1, 29.2.



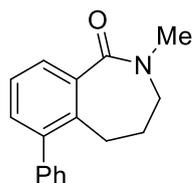
N-(4-Cyanobenzyl)tetrahydrobenzoazepin-1-one (**9ha**)<sup>[6]</sup> White powders (234 mg, 85%), m.p. = 112 – 113 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ(ppm): 7.72 – 7.70 (m, 1H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.40 – 7.32 (m, 2H), 7.13 (d, *J* = 7.2 Hz, 1H), 4.82 (s, 2H), 3.19 (t, *J* = 6.4 Hz, 2H), 2.75 (t, *J* = 7.2 Hz, 2H), 1.90 – 1.84 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ(ppm): 171.6, 143.7, 137.3, 135.5, 132.5, 131.2, 128.8, 128.8, 128.5, 127.2, 118.7, 111.5, 50.3, 46.2, 30.2, 29.2. IR (KBr.): ν(cm<sup>-1</sup>): 2223 (s, C≡N), 1637 (s, C=O).



N-(4-Formylbenzyl)tetrahydrobenzoazepin-1-one (**9ia**) White powders (75 mg, 27%; 201 mg, 72% by using 5 mol% Ni(OAc)<sub>2</sub>/2bpy), m.p. = 83 – 84 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ(ppm): 10.00 (s, 1H), 7.86 (d, *J* = 7.6 Hz, 2H), 7.72 (d, *J* = 6.8 Hz, 1H), 7.53 (d, *J* = 7.2 Hz, 2H), 7.37 – 7.33 (m, 2H), 7.12 (d, *J* = 6.4 Hz, 1H), 4.85 (s, 2H), 3.21 – 3.19 (m, 2H), 2.76 – 2.72 (m, 2H), 1.86 – 1.82 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ(ppm): 191.9, 171.7, 145.3, 137.4, 135.9, 135.6, 131.2, 130.3, 128.8, 128.8, 128.5, 127.2, 50.4, 46.2, 30.3, 29.3. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>18</sub>H<sub>18</sub>NO<sub>2</sub> 280.1338, found 280.1339. IR (KBr.): ν(cm<sup>-1</sup>): 1696 (s, C=O), 1635 (s, C=O).

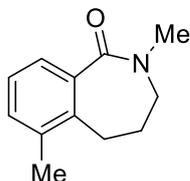


N-Phenyltetrahydrobenzoazepin-1-one (**9ja**) White powders (80 mg, 34%), m.p. = 94 – 95 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ(ppm): 7.76 (d, *J* = 7.2 Hz, 1H), 7.45 – 7.35 (m, 6H), 7.29 (t, *J* = 6.8 Hz, 1H), 7.20 (d, *J* = 7.2 Hz, 1H), 3.63 (t, *J* = 6.4 Hz, 2H), 2.99 (t, *J* = 7.2 Hz, 2H), 2.16 – 2.09 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ(ppm): 171.1, 143.1, 137.4, 136.3, 131.2, 129.3, 129.0, 128.3, 127.3, 126.8, 126.4, 49.7, 30.2, 29.9. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>16</sub>H<sub>16</sub>NO 238.1232, found 238.1234.

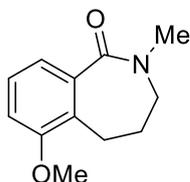


N-Methyl-6-phenyltetrahydrobenzoazepin-1-one (**9ka**) White powders (241 mg, 96%), m.p. = 145 – 146 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ(ppm): 7.57 – 7.53 (m, 1H), 7.33 – 7.26 (m, 3H), 7.25 – 7.22 (m, 2H), 7.17 – 7.15 (m, 2H), 3.19 (t, *J* = 6.4 Hz, 2H), 3.09 (s, 3H), 2.57 (t, *J* = 6.8 Hz, 2H), 1.91 – 1.84

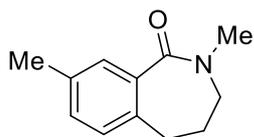
(m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ (ppm): 171.3, 141.3, 141.1, 137.4, 134.4, 132.1, 129.1, 128.2, 127.6, 127.2, 126.4, 48.0, 34.5, 29.5, 26.0. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{17}\text{H}_{18}\text{NO}$  252.1388, found 252.1389.



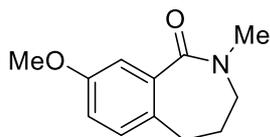
*N*,6-Dimethyltetrahydrobenzoazepin-1-one (**9la**) Colorless oil (157 mg, 83%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ (ppm): 7.44 (d,  $J = 7.2$  Hz, 1H), 7.20 (d,  $J = 7.2$  Hz, 1H), 7.15 (t,  $J = 7.6$  Hz, 1H), 3.16 – 3.13 (m (overlapped), 5H), 2.74 (t,  $J = 7.2$  Hz, 2H), 2.32 (s, 3H), 2.00 – 1.94 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ (ppm): 171.6, 137.0, 135.3, 134.6, 132.3, 126.5, 126.1, 48.0, 34.5, 28.1, 25.0, 19.7. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{12}\text{H}_{16}\text{NO}$  190.1232, found 190.1231.



*N*-Methyl-6-methoxytetrahydrobenzoazepin-1-one (**9ma**) White powders (186 mg, 91%), m.p. = 61 – 62 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ (ppm): 7.25 – 7.20 (m, 2H), 6.93 – 6.89 (m, 1H), 3.80 (s, 3H), 3.18 – 3.15 (m (overlapped), 5H), 2.83 (t,  $J = 6.8$  Hz, 2H), 2.00 – 1.93 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ (ppm): 171.0, 155.9, 138.0, 127.4, 125.6, 120.3, 112.6, 55.8, 48.2, 34.4, 28.1, 20.7. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{12}\text{H}_{16}\text{NO}_2$  206.1181, found 206.1180.

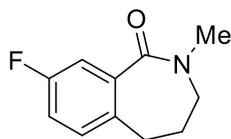


*N*,8-Dimethyltetrahydrobenzoazepin-1-one (**9na**)<sup>[4]</sup> Colorless oil (153 mg, 81%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ (ppm): 7.46 (s, 1H), 7.14 (dd,  $J = 7.6, 0.8$  Hz, 1H), 6.99 (d,  $J = 7.6$  Hz, 1H), 3.19 (t,  $J = 6.4$  Hz, 2H), 3.16 (s, 3H), 2.71 (t,  $J = 7.2$  Hz, 2H), 2.33 (s, 3H), 2.04 – 1.97 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ (ppm): 171.5, 136.6, 136.2, 134.4, 131.4, 129.0, 128.2, 48.2, 34.6, 29.7, 28.9, 21.0.

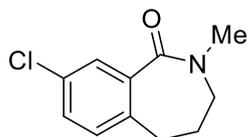


*N*-Methyl-8-methoxytetrahydrobenzoazepin-1-one (**9oa**) Colorless oil (195 mg, 95%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ (ppm): 7.18 (d,  $J = 2.8$  Hz, 1H), 7.00 (d,  $J = 8.4$  Hz, 1H), 6.87 (dd,  $J = 8.4, 2.8$  Hz, 1H),

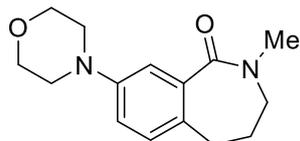
3.78 (s, 3H), 3.18 (t,  $J = 6.4$  Hz, 2H), 3.14 (s, 3H), 2.68 (t,  $J = 6.8$  Hz, 2H), 2.01 – 1.95 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ (ppm): 171.0, 158.5, 137.1, 129.5, 129.3, 117.0, 112.9, 55.3, 48.1, 34.5, 29.0, 28.8. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{12}\text{H}_{16}\text{NO}_2$  206.1181, found 206.1183.



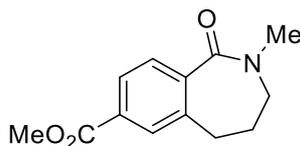
N-Methyl-8-fluorotetrahydrobenzoazepin-1-one (**9pa**) Colorless oil (179 mg, 93%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ (ppm): 7.34 – 7.31 (m, 1H), 7.08 – 7.05 (m, 1H), 7.02 – 6.98 (m, 1H), 3.18 (t,  $J = 6.4$  Hz, 2H), 3.14 (s, 3H), 2.70 (t,  $J = 7.2$  Hz, 2H), 2.04 – 1.97 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ (ppm): 169.7 (d,  $J = 2.0$  Hz), 161.5 (d,  $J = 244$  Hz), 137.9 (d,  $J = 7.0$  Hz), 133.0 (d,  $J = 4.0$  Hz), 129.8 (d,  $J = 8.0$  Hz), 117.2 (d,  $J = 2.1$  Hz), 115.1 (d,  $J = 2.3$  Hz), 47.8, 34.4, 29.1, 28.5. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{11}\text{H}_{13}\text{FNO}$  194.0981, found 194.0982.



N-Methyl-8-chlorotetrahydrobenzoazepin-1-one (**9qa**) Colorless oil (179 mg, 86%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ (ppm): 7.61 (d,  $J = 2.4$  Hz, 1H), 7.29 (dd,  $J = 8.0, 2.4$  Hz, 1H), 7.05 (d,  $J = 8.0$  Hz, 1H), 3.19 (t,  $J = 6.4$  Hz, 2H), 3.15 (s, 3H), 2.72 (t,  $J = 7.2$  Hz, 2H), 2.05 – 1.99 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ (ppm): 169.5, 137.7, 135.6, 132.5, 130.4, 129.6, 128.2, 47.7, 34.4, 29.3, 28.4. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{11}\text{H}_{13}\text{ClNO}$  210.0686, found 210.0687.

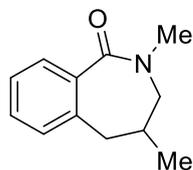


N-Methyl-8-morpholinotetrahydrobenzoazepin-1-one (**9ra**) Colorless oil (185 mg, 71%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ (ppm): 7.19 (d,  $J = 2.4$  Hz, 1H), 7.00 (d,  $J = 8.4$  Hz, 1H), 6.87 (dd,  $J = 8.4, 2.8$  Hz, 1H), 3.82 – 3.80 (m, 4H), 3.19 – 3.12 (m (overlapped), 9H), 2.66 (t,  $J = 6.8$  Hz, 2H), 2.00 – 1.93 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ (ppm): 171.5, 150.2, 136.9, 129.1, 128.8, 117.9, 115.5, 66.9, 49.3, 48.2, 34.6, 29.1, 28.9. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{15}\text{H}_{21}\text{N}_2\text{O}_2$  261.1603, found 261.1604.

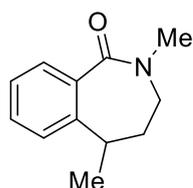


N-Methyl-7-(methoxycarbonyl)tetrahydrobenzoazepin-1-one (**9sa**) White powders (140 mg, 60%), m.p. = 96 – 97 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ (ppm): 7.94 (dd,  $J = 8.0, 1.2$  Hz, 1H), 7.80 (s, 1H),

7.69 (d,  $J = 8.0$  Hz, 1H), 3.89 (s, 3H), 3.19 – 3.15 (m (overlapped), 5H), 2.79 (t,  $J = 6.8$  Hz, 2H), 2.07 – 2.00 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ (ppm): 170.0, 166.4, 140.4, 137.4, 131.8, 129.3, 128.4, 128.0, 52.1, 47.7, 34.4, 29.8, 28.4. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{13}\text{H}_{16}\text{NO}_3$  234.1130, found 234.1131. IR (KBr):  $\nu(\text{cm}^{-1})$ : 1719 (s, C=O), 1635 (s, C=O).

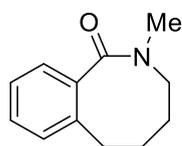


N,4-Dimethyltetrahydrobenzoazepin-1-one (**9af**) White powders (174 mg, 92%), m.p. = 62 – 63 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ (ppm): 7.66 – 7.64 (m, 1H), 7.34 – 7.28 (m, 2H), 7.09 – 7.07 (m, 1H), 3.18 – 3.12 (m (overlapped), 4H), 2.98 – 2.78 (m, 2H), 2.42 – 2.38 (m, 2H), 0.95 (d,  $J = 6.4$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ (ppm): 171.2, 136.4, 136.2, 130.4, 128.9, 128.4, 126.9, 54.8, 38.1, 35.8, 35.4, 18.1. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{12}\text{H}_{16}\text{NO}$  190.1232, found 190.1234.

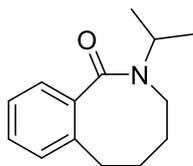


N,5-Dimethyltetrahydrobenzoazepin-1-one (**9ag**) Colorless oil (102 mg, 54%).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.60 (d,  $J = 7.2$  Hz, 1H), 7.40 – 7.37 (m, 1H), 7.29 – 7.27 (m, 1H), 7.19 (d,  $J = 7.8$  Hz, 1H), 3.22 – 3.17 (m, 1H), 3.15 (s, 3H), 3.11 – 3.07 (m, 1H), 3.05 – 3.00 (m, 1H), 2.37 – 2.33 (m, 1H), 1.47 – 1.41 (m, 1H), 1.34 (d,  $J = 7.2$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ (ppm): 171.4, 136.5, 136.1, 134.3, 131.4, 128.9, 128.2, 48.1, 34.5, 29.6, 28.8, 20.9. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{12}\text{H}_{16}\text{NO}$  190.1232, found 190.1234.

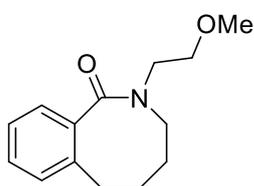
### Characterization data for tetrahydrobenzoazocin-1(2H)-ones



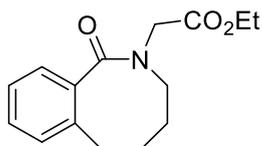
N-Methyltetrahydrobenzoazocin-1(2H)-one (**10aa**)<sup>[7]</sup> White powders (149 mg, 79%; 125 mg, 66% from **5b**), m.p. = 36 – 37 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ (ppm): 7.39 – 7.37 (m, 1H), 7.34 – 7.30 (m, 1H), 7.24 – 7.20 (m, 1H), 7.14 (d,  $J = 7.6$  Hz, 1H), 3.34 – 3.28 (m, 1H), 3.12 (s, 3H), 3.08 – 3.03 (m, 1H), 2.81 – 2.76 (m, 1H), 2.66 – 2.60 (m, 1H), 2.10 – 2.04 (m, 1H), 1.80 – 1.64 (m, 2H), 1.54 – 1.43 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ (ppm): 171.0, 140.2, 135.5, 130.1, 129.2, 127.2, 126.4, 49.8, 33.2, 32.4, 27.7, 25.7.



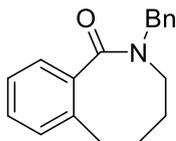
N-Isopropyltetrahydrobenzoazocin-1(2H)-one (**10ca**)<sup>[8]</sup> White powders (46 mg, 21%), m.p. = 74 – 75 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ(ppm): 7.35 (d, *J* = 7.2 Hz, 1H), 7.32 – 7.28 (m, 1H), 7.22 – 7.19 (m, 1H), 7.12 (d, *J* = 7.6 Hz, 1H), 4.71 – 4.61 (m, 1H), 3.24 – 3.19 (m, 1H), 3.11 – 3.04 (m, 1H), 2.81 – 2.71 (m, 2H), 2.10 – 2.02 (m, 1H), 1.77 – 1.69 (m, 2H), 1.47 – 1.38 (m, 1H), 1.35 (d, *J* = 7.2 Hz, 3H), 1.28 (d, *J* = 6.8 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ(ppm): 171.3, 140.0, 136.6, 130.0, 129.2, 127.7, 126.4, 47.4, 43.9, 32.4, 28.7, 27.7, 21.2, 20.0.



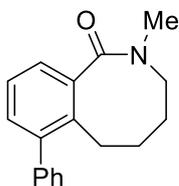
N-(2-Methoxy)ethyltetrahydrobenzoazocin-1(2H)-one (**10da**) Colorless oil (135 mg, 58%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ(ppm): 7.38 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.34 – 7.29 (m, 1H), 7.24 – 7.20 (m, 1H), 7.13 (d, *J* = 7.6 Hz, 1H), 3.99 – 3.93 (m, 1H), 3.70 – 3.68 (m, 2H), 3.45 – 3.38 (m, 1H), 3.36 (s, 3H), 3.33 – 3.18 (m, 2H), 2.82 – 2.74 (m, 1H), 2.68 – 2.62 (m, 1H), 2.09 – 2.03 (m, 1H), 1.81 – 1.73 (m, 1H), 1.68 – 1.62 (m, 1H), 1.51 – 1.40 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ(ppm): 171.2, 140.2, 135.5, 130.2, 129.2, 127.4, 126.4, 70.8, 58.8, 48.9, 46.0, 32.3, 27.6, 26.2. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>14</sub>H<sub>20</sub>NO<sub>2</sub> 234.1494, found 234.1495.



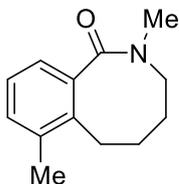
N-(2-Ethoxy-2-oxoethyl)tetrahydrobenzoazocin-1(2H)-one (**10fa**) Colorless oil (91 mg, 35%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ(ppm): 7.42 (d, *J* = 7.6 Hz, 1H), 7.36 – 7.32 (m, 1H), 7.26 – 7.22 (m, 1H), 7.16 (d, *J* = 7.6 Hz, 1H), 4.33 (d, *J* = 16.8 Hz, 1H), 4.25 – 4.20 (m, 2H), 4.12 (d, *J* = 16.8 Hz, 1H), 3.42 – 3.35 (m, 1H), 3.17 – 3.11 (m, 1H), 2.96 – 2.89 (m, 1H), 2.81 – 2.75 (m, 1H), 2.14 – 2.07 (m, 1H), 1.81 – 1.63 (m, 2H), 1.55 – 1.44 (m, 1H), 1.29 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ(ppm): 171.5, 169.3, 140.7, 134.6, 130.5, 129.4, 127.6, 126.5, 61.3, 49.5, 48.5, 31.8, 27.7, 26.0, 14.2. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>15</sub>H<sub>20</sub>NO<sub>3</sub> 262.1443, found 262.1444. IR (KBr): ν(cm<sup>-1</sup>): 1745 (s, C=O), 1635 (s, C=O).



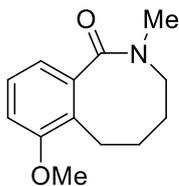
N-Benzyltetrahydrobenzoazocin-1(2H)-one (**10ga**) Colorless oil (173 mg, 65%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ (ppm): 7.50 – 7.48 (m, 1H), 7.38 – 7.34 (m, 5H), 7.31 – 7.26(m, 2H), 7.18 (d,  $J$  = 7.6 Hz, 1H), 5.49 (d,  $J$  = 14.8 Hz, 1H), 4.17 (d,  $J$  = 14.8 Hz, 1H), 3.20 – 3.07 (m, 2H), 2.87 – 2.82 (m, 1H), 2.78 – 2.72 (m, 1H), 2.12 – 2.07 (m, 1H), 1.80 – 1.63 (m, 2H), 1.55 – 1.45 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ (ppm): 171.4, 140.2, 137.4, 135.4, 130.3, 129.3, 128.6, 128.2, 127.5, 127.4, 126.5, 48.1, 46.4, 32.4, 27.9, 25.9. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{18}\text{H}_{20}\text{NO}$  266.1545, found 266.1546.



N-Methyl-7-phenyltetrahydrobenzoazocin-1(2H)-one (**10ka**) White powders (167 mg, 63%), m.p. = 125 – 126 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ (ppm): 7.35 – 7.26 (m, 4H), 7.23 – 7.14 (m, 4H), 3.41 – 3.34 (m, 1H), 3.08 – 3.02 (m (overlapped), 4H), 2.87 – 2.81 (m, 1H), 2.35 – 2.29 (m, 1H), 1.67 – 1.55 (m, 3H), 1.32 – 1.22 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ (ppm): 171.3, 141.9, 141.5, 137.4, 136.5, 131.6, 129.2, 128.1, 127.0, 126.3, 126.1, 49.8, 33.2, 28.0, 26.8, 25.6. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{18}\text{H}_{20}\text{NO}$  266.1545, found 266.1547.

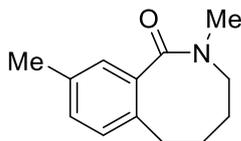


N,7-Dimethyltetrahydrobenzoazocin-1(2H)-one (**10la**) White powders (138 mg, 68%), m.p. = 74 – 75 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ (ppm): 7.22 – 7.18 (m, 2H), 7.15 – 7.11 (m, 1H), 3.36 (dd,  $J$  = 14.8, 11.2 Hz, 1H), 3.12 (s, 3H), 3.05 (dd,  $J$  = 14.8, 5.6 Hz, 1H), 2.90 (dd,  $J$  = 14.0, 8.0 Hz, 1H), 2.51 – 2.45 (m, 1H), 2.31 (s, 3H), 2.08 – 2.01 (m, 1H), 1.83 – 1.72 (m, 1H), 1.70 – 1.63 (m, 1H), 1.50 – 1.39 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ (ppm): 171.6, 138.1, 136.1, 135.5, 131.8, 126.4, 124.9, 49.8, 33.2, 28.1, 25.5, 25.4, 19.5. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{13}\text{H}_{18}\text{NO}$  204.1388, found 204.1390.

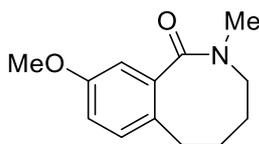


N-Methyl-7-methoxytetrahydrobenzoazocin-1(2H)-one (**10ma**) White powders (147 mg, 67%), m.p. =

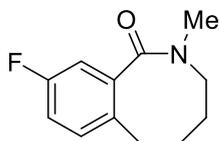
110 – 111 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ(ppm): 7.19 (t, *J* = 8.0 Hz, 1H), 6.97 (d, *J* = 7.6 Hz, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 3.81 (s, 3H), 3.37 – 3.30 (m, 1H), 3.17 – 3.12 (m, 1H), 3.10 (s, 3H), 3.04 – 2.99 (m, 1H), 2.27 – 2.20 (m, 1H), 2.00 – 1.93 (m, 1H), 1.78 – 1.67 (m, 1H), 1.66 – 1.59 (m, 1H), 1.44 – 1.36 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ(ppm): 170.9, 156.4, 136.9, 128.7, 127.4, 119.0, 111.4, 55.6, 49.9, 33.2, 25.7, 25.4, 24.8. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>13</sub>H<sub>18</sub>NO<sub>2</sub> 220.1338, found 220.1339.



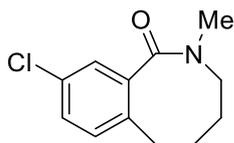
N,9-Dimethyltetrahydrobenzoazocin-1(2H)-one (**10na**)<sup>[8]</sup> White powders (121 mg, 60%), m.p. = 84 – 85 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ(ppm): 7.18 (s, 1H), 7.11 (d, *J* = 8.0 Hz, 1H), 7.01 (d, *J* = 7.6 Hz, 1H), 3.35 – 3.28 (m, 1H), 3.09 (s, 3H), 3.06 – 3.01 (m, 1H), 2.73 (dd, *J* = 13.6, 7.6 Hz, 1H), 2.60 – 2.54 (m, 1H), 2.29 (s, 3H), 2.08 – 2.00 (m, 1H), 1.77 – 1.63 (m, 2H), 1.49 – 1.38 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ(ppm): 171.3, 137.3, 136.0, 135.3, 130.9, 129.2, 127.6, 49.8, 33.2, 31.9, 27.9, 25.8, 20.8.



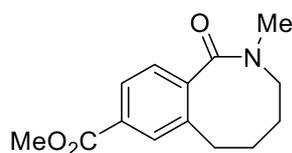
N-Methyl-9-methoxytetrahydrobenzoazocin-1(2H)-one (**10oa**) Colorless oil (151 mg, 70%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ(ppm): 7.03 (d, *J* = 8.4 Hz, 1H), 6.90 (d, *J* = 2.4 Hz, 1H), 6.86 (dd, *J* = 8.4, 2.4 Hz, 1H), 3.77 (s, 3H), 3.36 – 3.30 (m, 1H), 3.10 (s, 3H), 3.06 – 3.01 (m, 1H), 2.75 – 2.70 (m, 1H), 2.58 – 2.51 (m, 1H), 2.04 – 2.00 (m, 1H), 1.77 – 1.64 (m, 2H), 1.48 – 1.37 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ(ppm): 170.9, 158.0, 136.2, 132.5, 130.5, 116.9, 111.3, 55.3, 49.8, 33.2, 31.5, 27.9, 25.7. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>13</sub>H<sub>18</sub>NO<sub>2</sub> 220.1338, found 220.1336.



N-Methyl-9-fluorotetrahydrobenzoazocin-1(2H)-one (**10pa**) White powders (130 mg, 63%), m.p. = 54 – 55 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ(ppm): 7.11 – 7.06 (m, 2H), 7.02 – 6.97 (m, 1H), 3.33 – 3.26 (m, 1H), 3.10 – 3.04 (m (overlapped), 4H), 2.79 – 2.73 (m, 1H), 2.61 – 2.54 (m, 1H), 2.08 – 2.03 (m, 1H), 1.78 – 1.64 (m, 2H), 1.49 – 1.38 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ(ppm): 169.6, 160.1 (d, *J* = 40.0 Hz), 137.0 (d, *J* = 7.0 Hz), 136.1 (d, *J* = 3.0 Hz), 131.0 (d, *J* = 7.5 Hz), 117.0 (d, *J* = 21.0 Hz), 113.9 (d, *J* = 22.0 Hz), 49.7, 33.2, 31.5, 27.6, 25.6. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>12</sub>H<sub>15</sub>FNO 208.1138, found 208.1140.



N-Methyl-9-chlorotetrahydrobenzoazocin-1(2H)-one (**10qa**) Colorless oil (105 mg, 47%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ (ppm): 7.31 (d,  $J = 2.0$  Hz, 1H), 7.22 (dd,  $J = 8.0, 2.0$  Hz, 1H), 7.03 (d,  $J = 8.0$  Hz, 1H), 3.27 – 3.21 (m, 1H), 3.05 – 2.99 (m (overlapped), 4H), 2.73 – 2.68 (m, 1H), 2.57 – 2.50 (m, 1H), 2.04 – 1.97 (m, 1H), 1.73 – 1.60 (m, 2H), 1.44 – 1.33 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ (ppm): 169.5, 138.7, 137.0, 132.0, 130.7, 130.1, 127.2, 49.7, 33.2, 31.8, 27.5, 25.6. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{12}\text{H}_{15}\text{ClNO}$  224.0842, found 224.0843.



N-Methyl-8-(methoxycarbonyl)tetrahydrobenzoazocin-1(2H)-one (**10sa**) White powders (52 mg, 21%), m.p. = 101 – 102 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ (ppm): 7.87 (dd,  $J = 8.0, 1.6$  Hz, 1H), 7.83 (s, 1H), 7.43 (d,  $J = 8.0$  Hz, 1H), 3.88 (s, 3H), 3.26 – 3.19 (m, 1H), 3.10 (s, 3H), 3.08 – 3.03 (m, 1H), 2.87 – 2.82 (m, 1H), 2.67 – 2.61 (m, 1H), 2.12 – 2.07 (m, 1H), 1.76 – 1.64 (m, 2H), 1.53 – 1.42 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  170.0, 166.5, 140.5, 139.8, 131.5, 130.5, 127.6, 127.4, 52.2, 49.7, 33.2, 32.2, 27.6, 25.6. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{14}\text{H}_{18}\text{NO}_3$  248.1287, found 248.1289. IR (KBr):  $\nu(\text{cm}^{-1})$ : 1719 (s, C=O), 1625 (s, C=O).

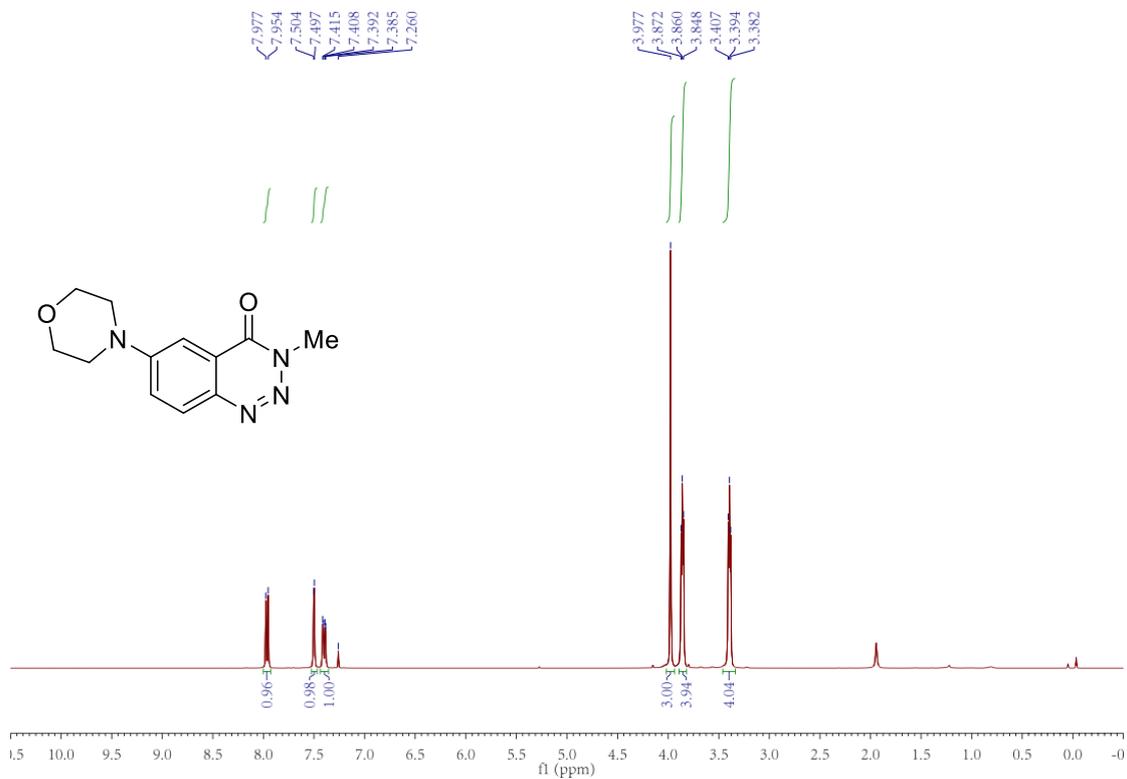
## References

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2. Kurouchi, H.; Kawamoto, K.; Sugimoto, H.; Nakamura, S.; Otani, Y.; Ohwada, T. *J. Org. Chem.* **2012**, *77*, 9313–9328.
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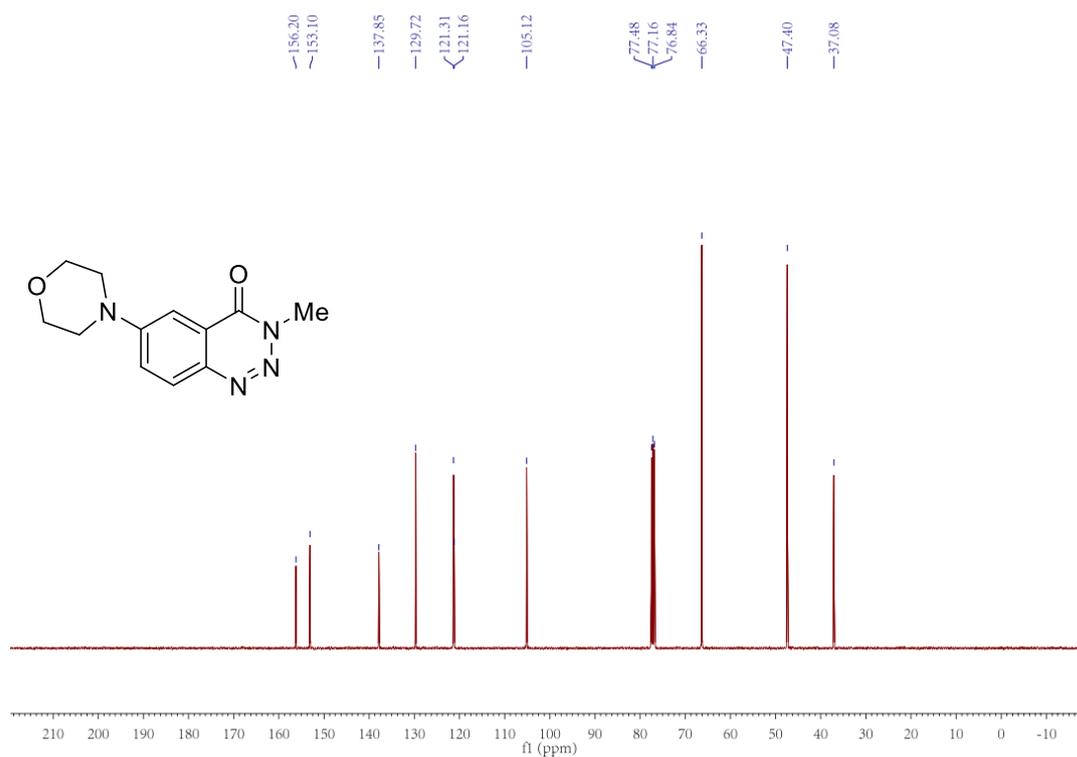
## $^1\text{H}$ and $^{13}\text{C}$ NMR Spectra

### 3-Methyl-6-morpholinobenzo[d][1,2,3]triazin-4(3H)-one (**1r**)

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )

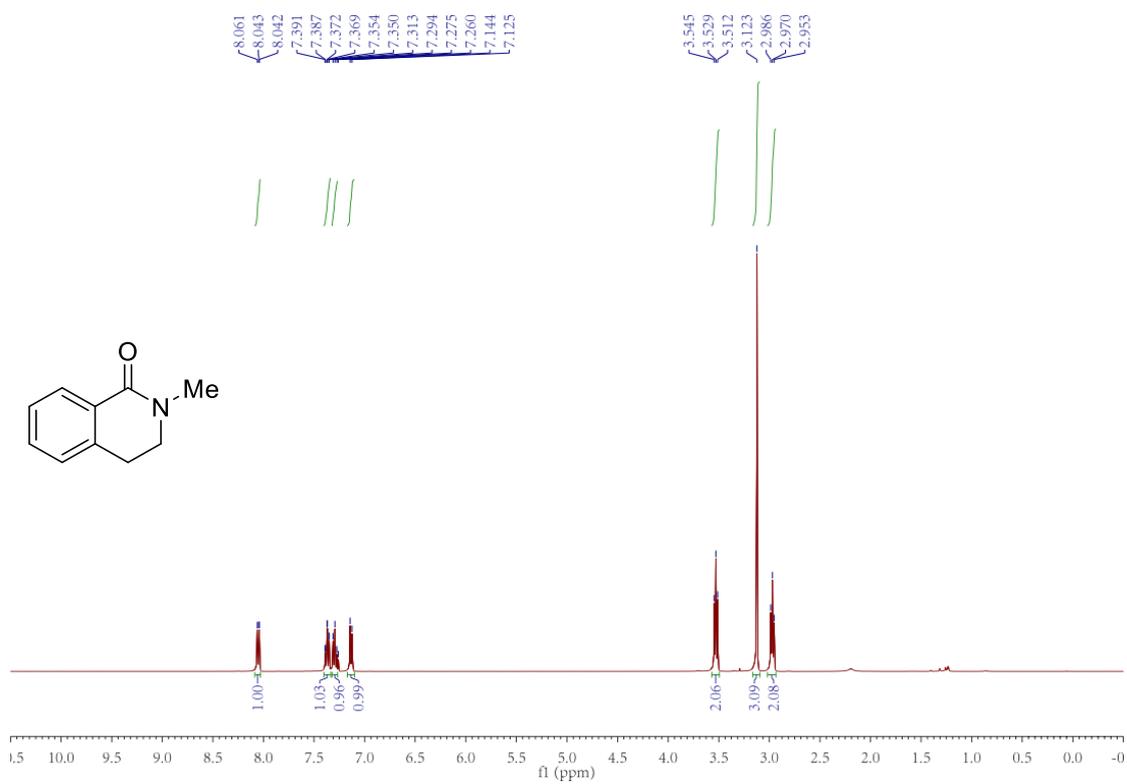


$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

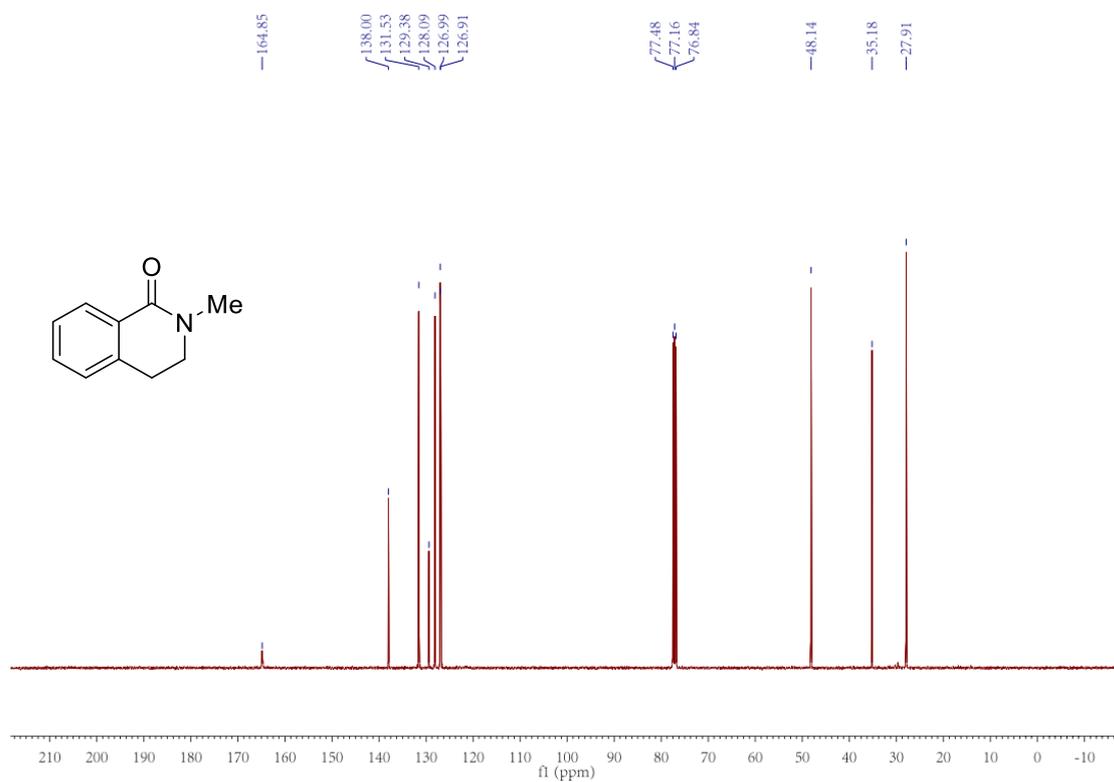


2-Methyl-3,4-dihydroisoquinolin-1(2H)-one (**8aa**)

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )

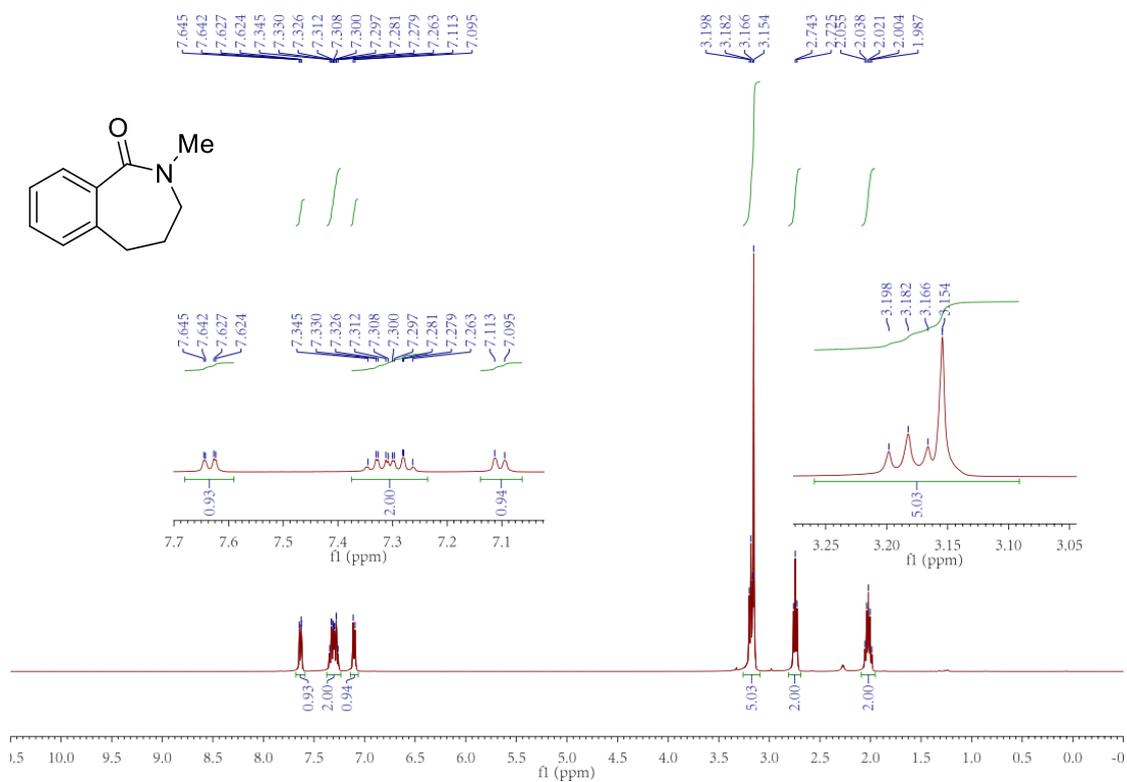


$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

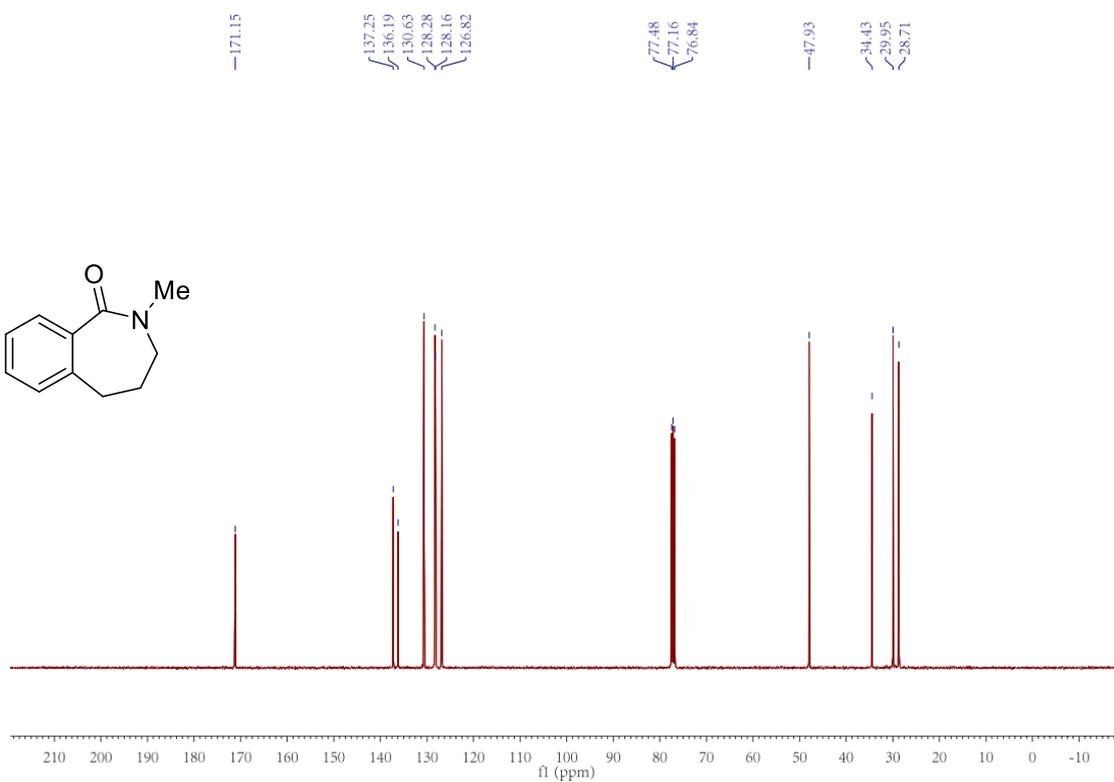


# N-Methyltetrahydrobenzoazepin-1-one (9aa)

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )

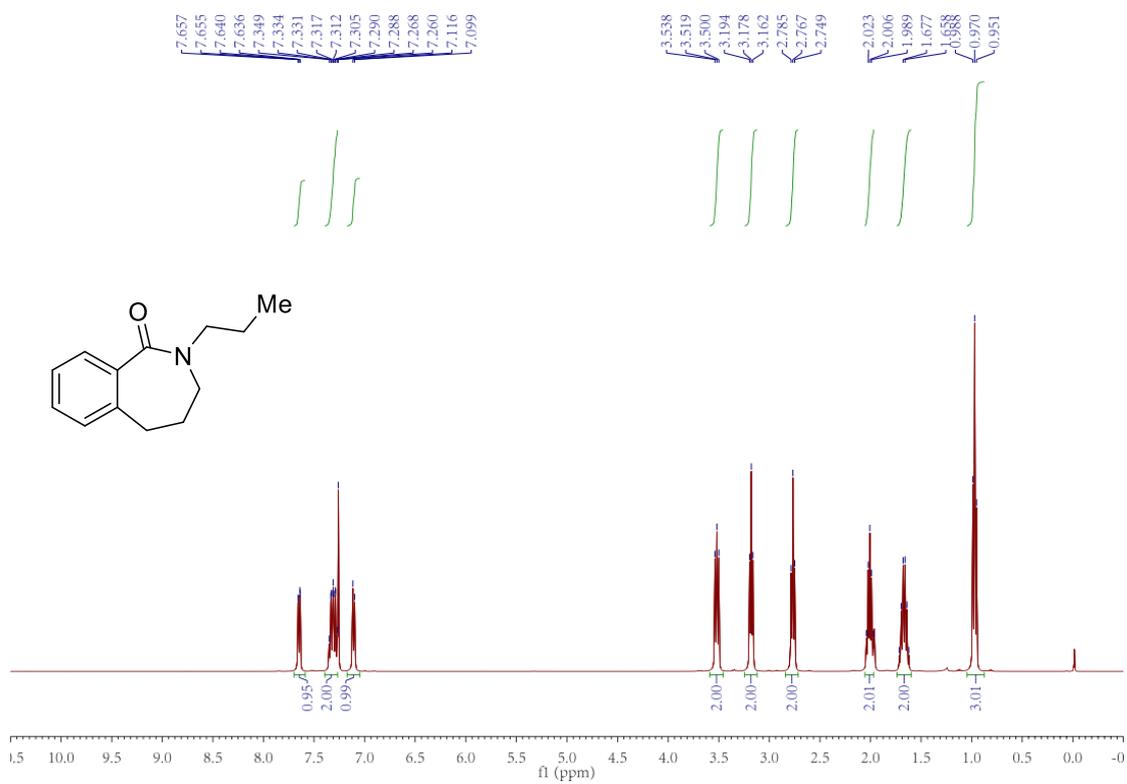


$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

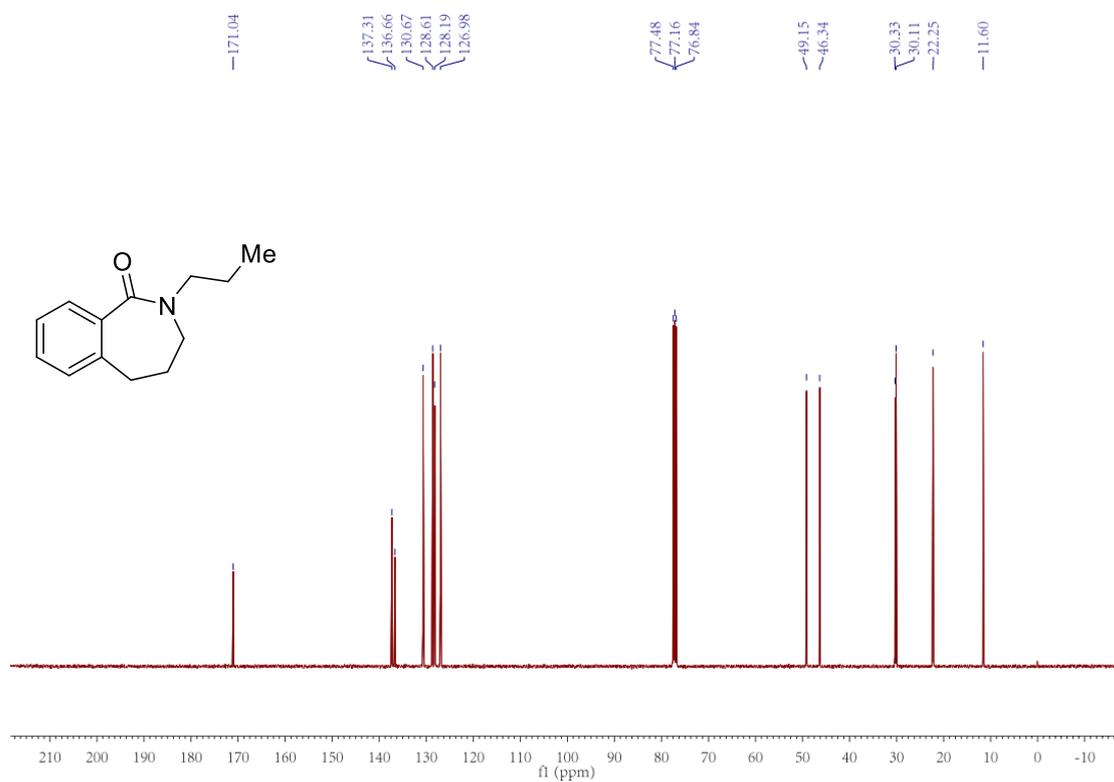


N-Propyltetrahydrobenzoazepin-1-one (**9ba**)

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )

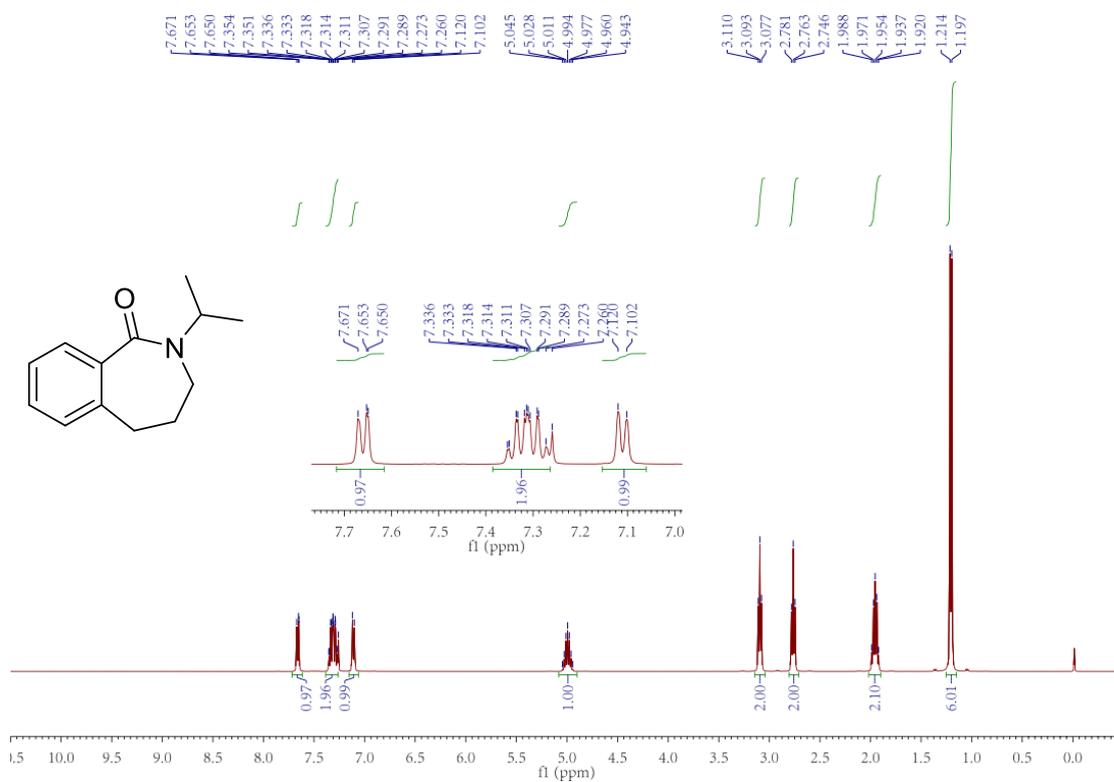


$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

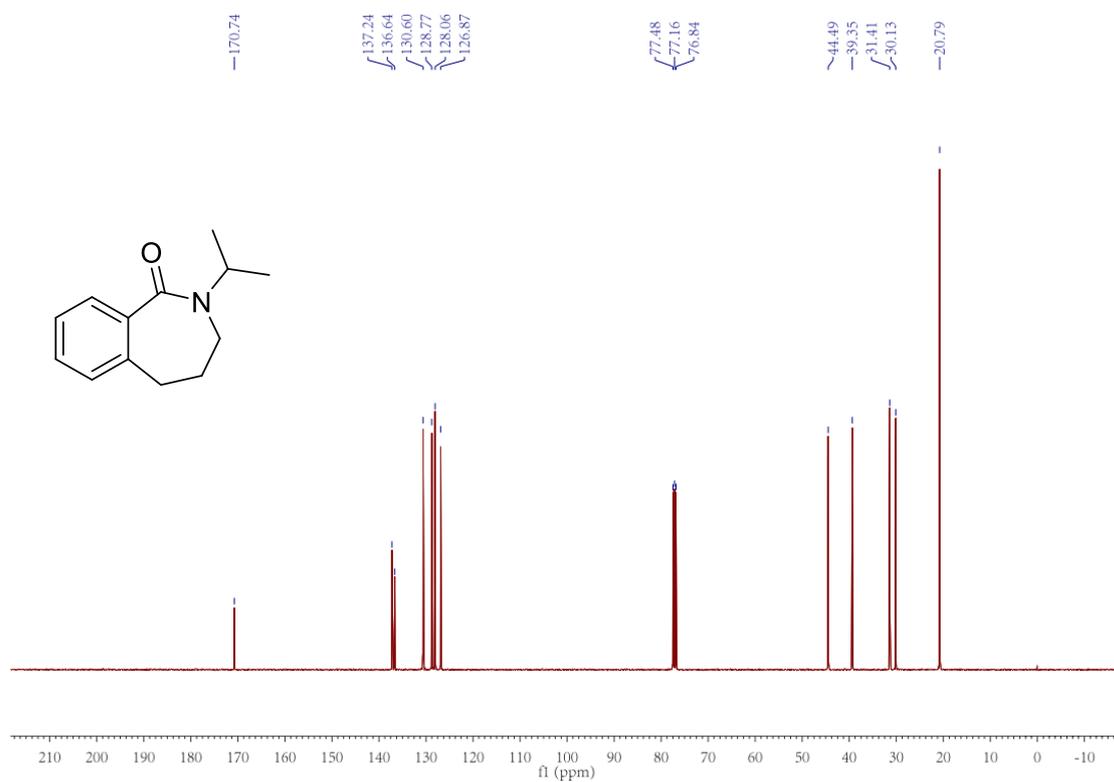


# N-Isopropyltetrahydrobenzoazepin-1-one (9ca)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

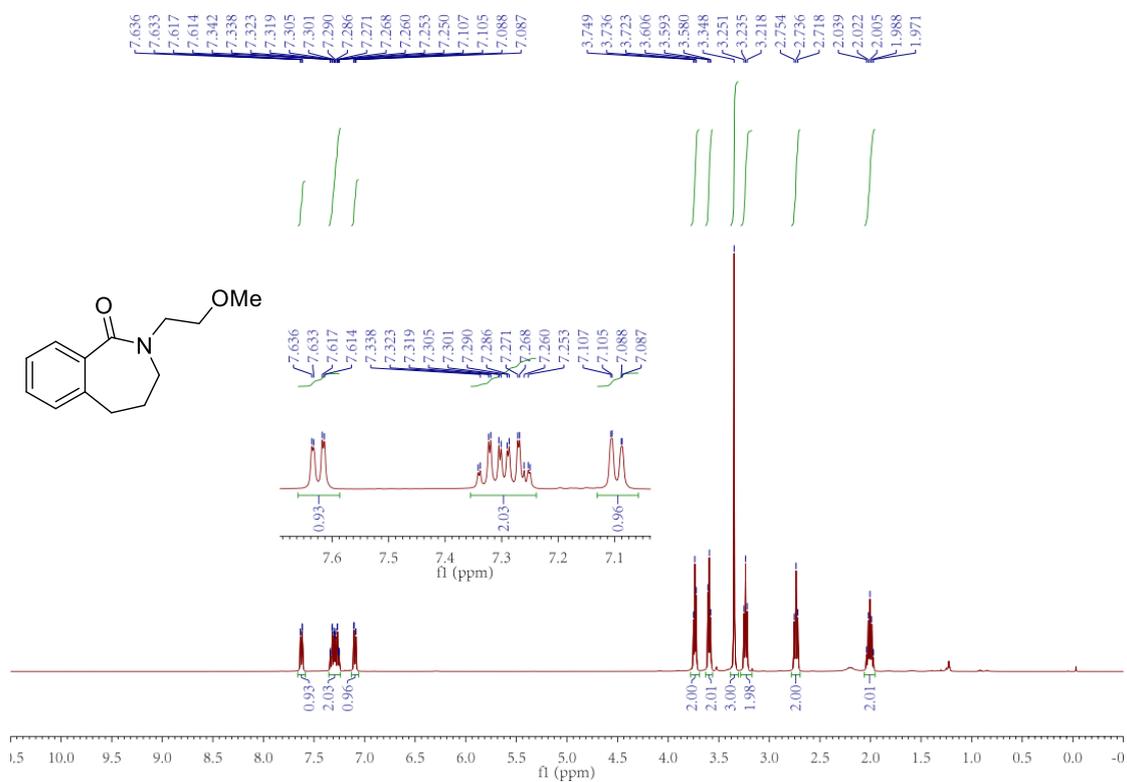


<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

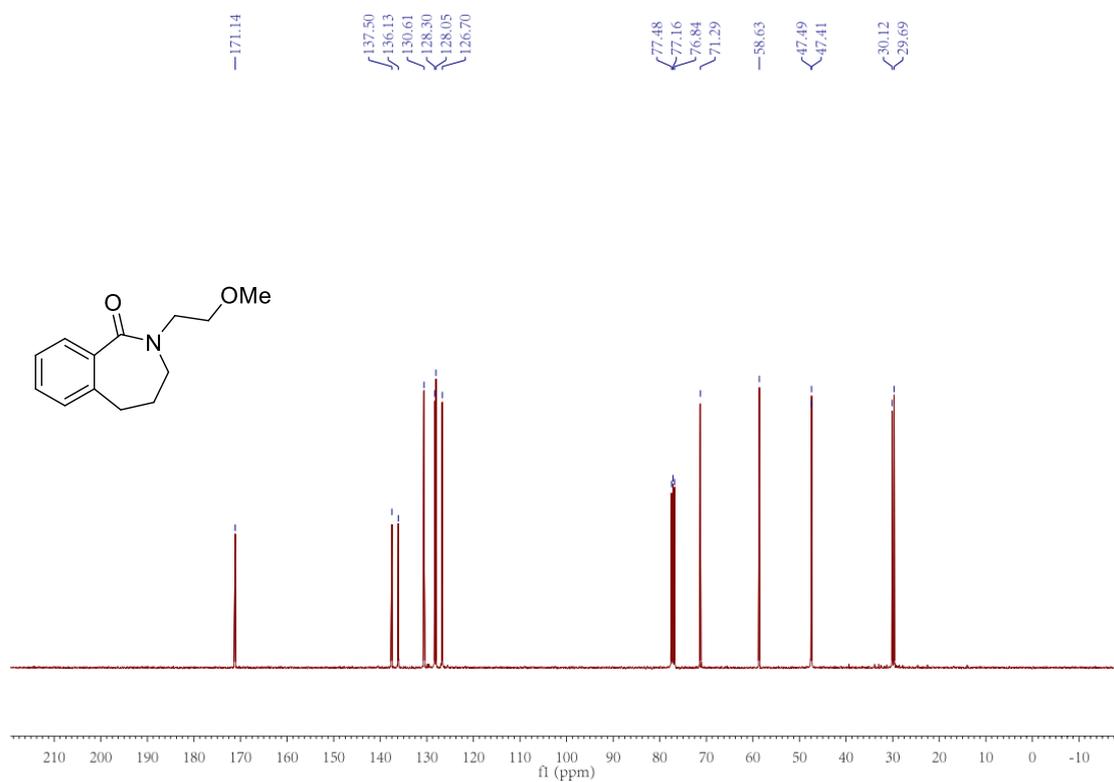


N-(2-Methoxyethyl)tetrahydrobenzoazepin-1-one (**9da**)

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )

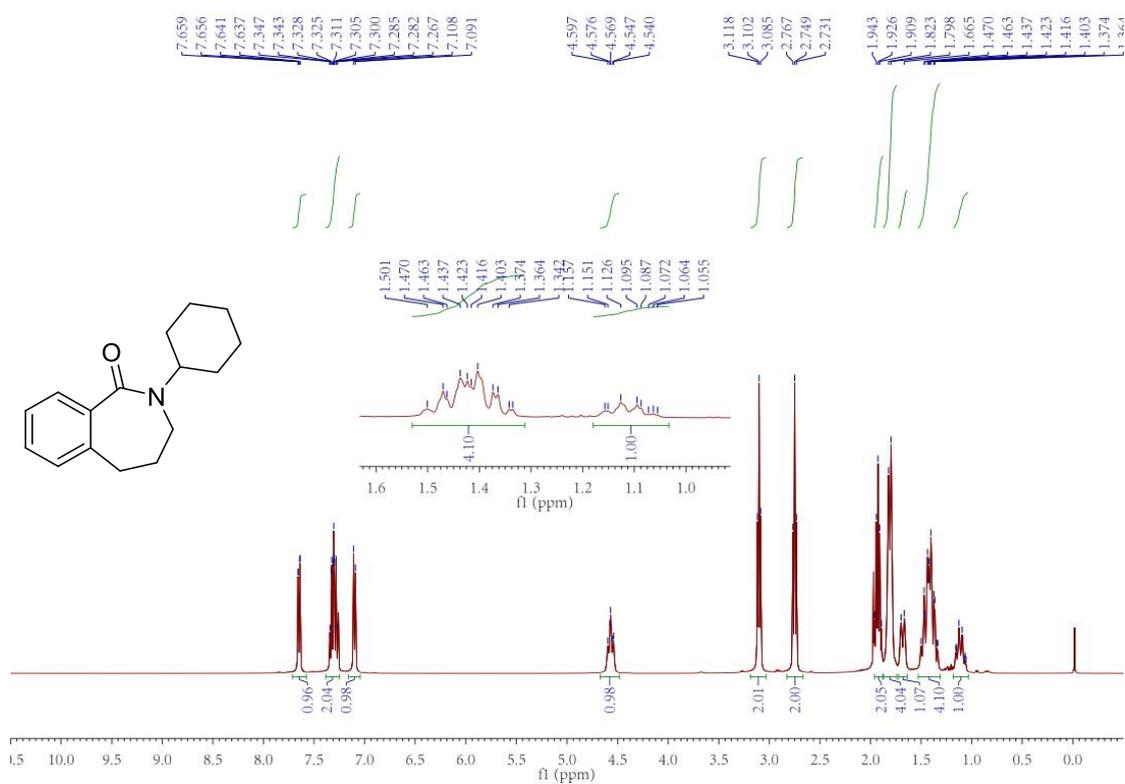


$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

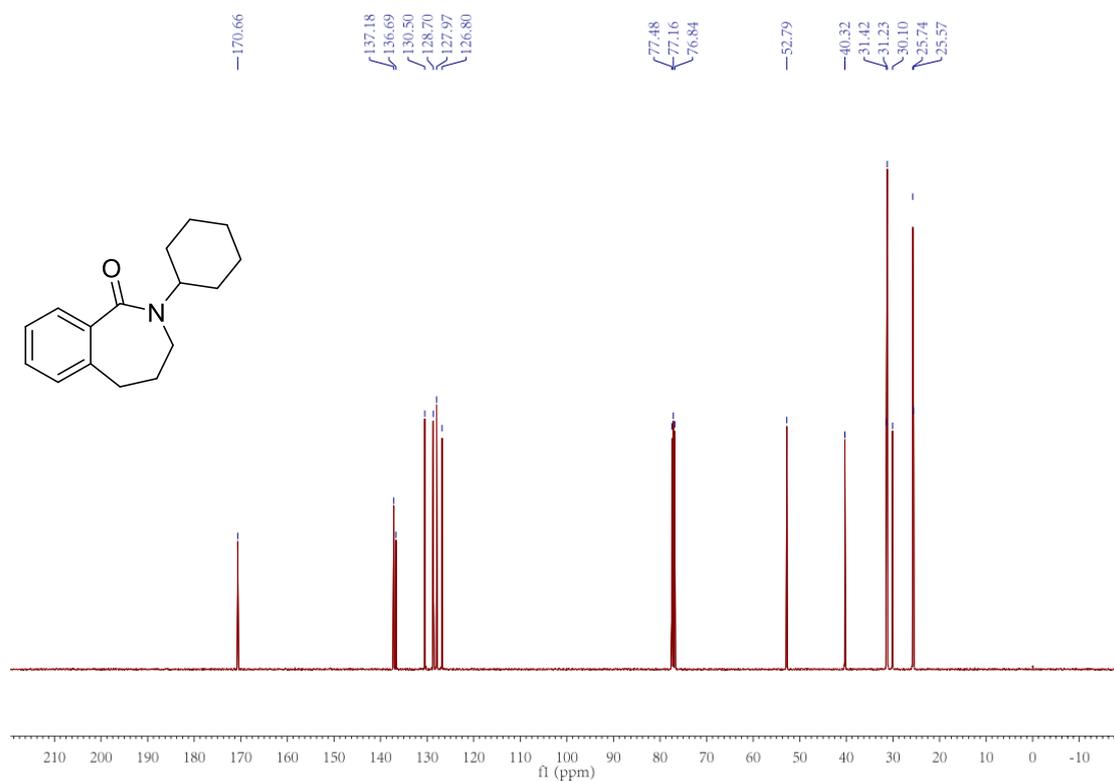


N-Cyclohexyltetrahydrobenzoazepin-1-one (**9ea**)

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )

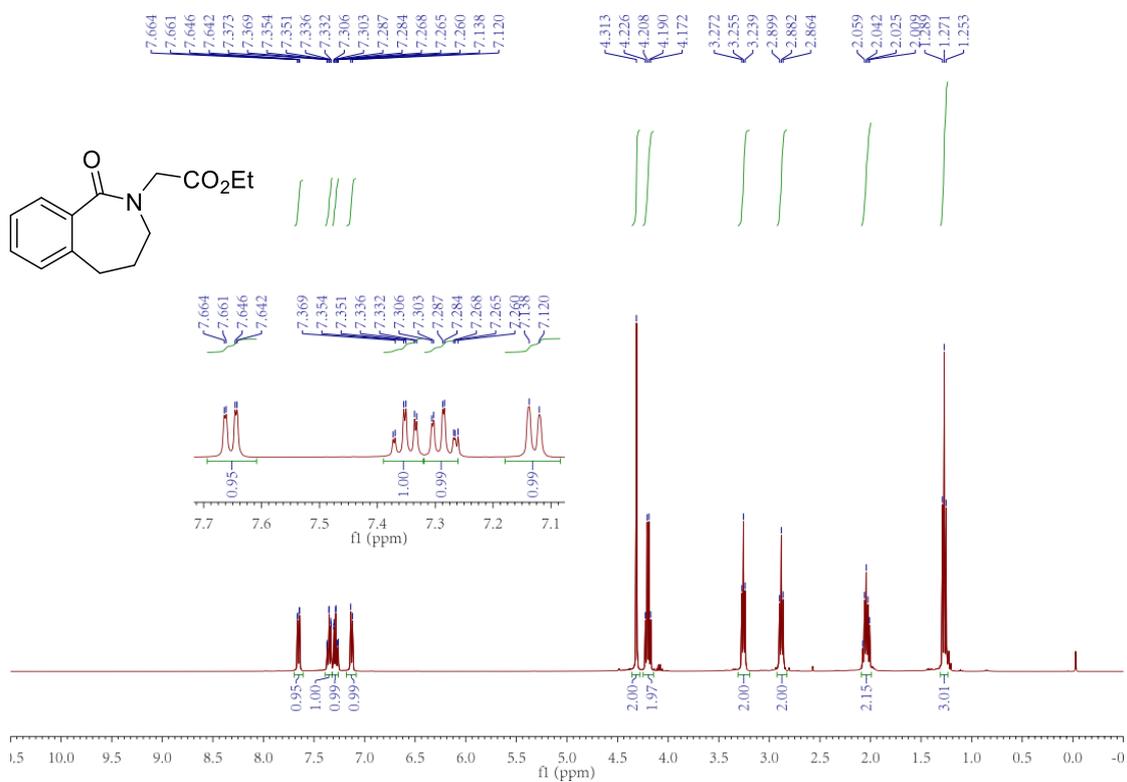


$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

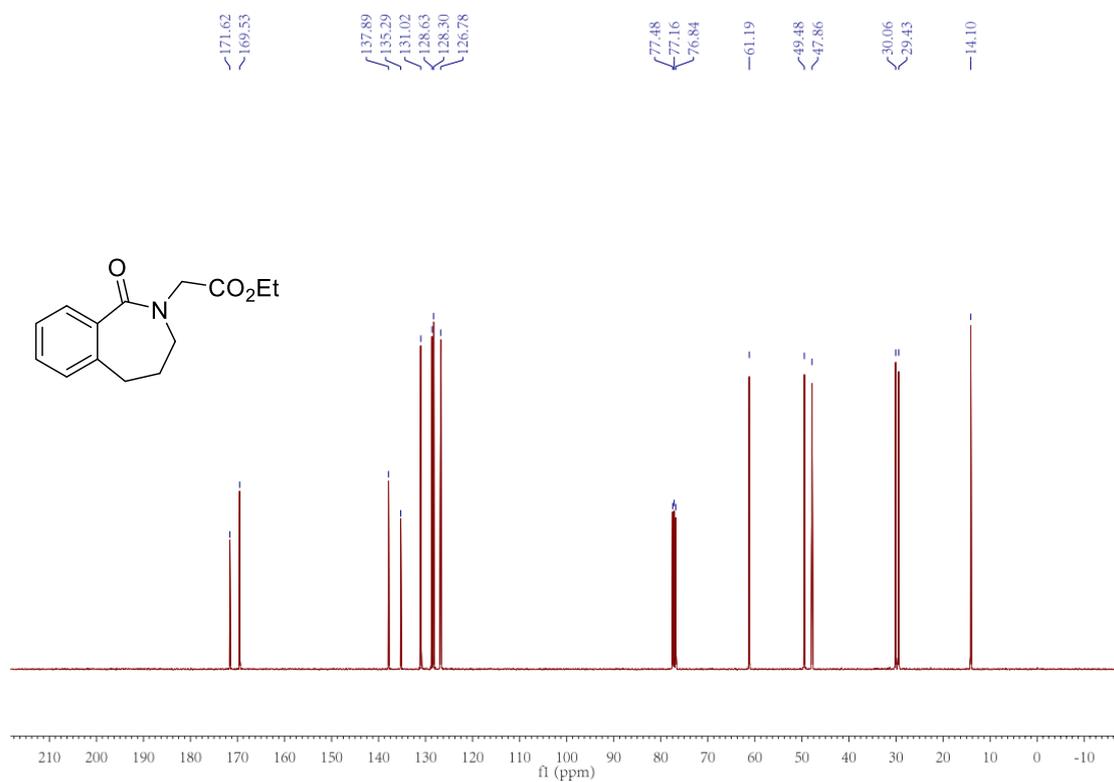


N-(2-Ethoxy-2-oxoethyl)tetrahydrobenzoozepin-1-one (**9fa**)

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )

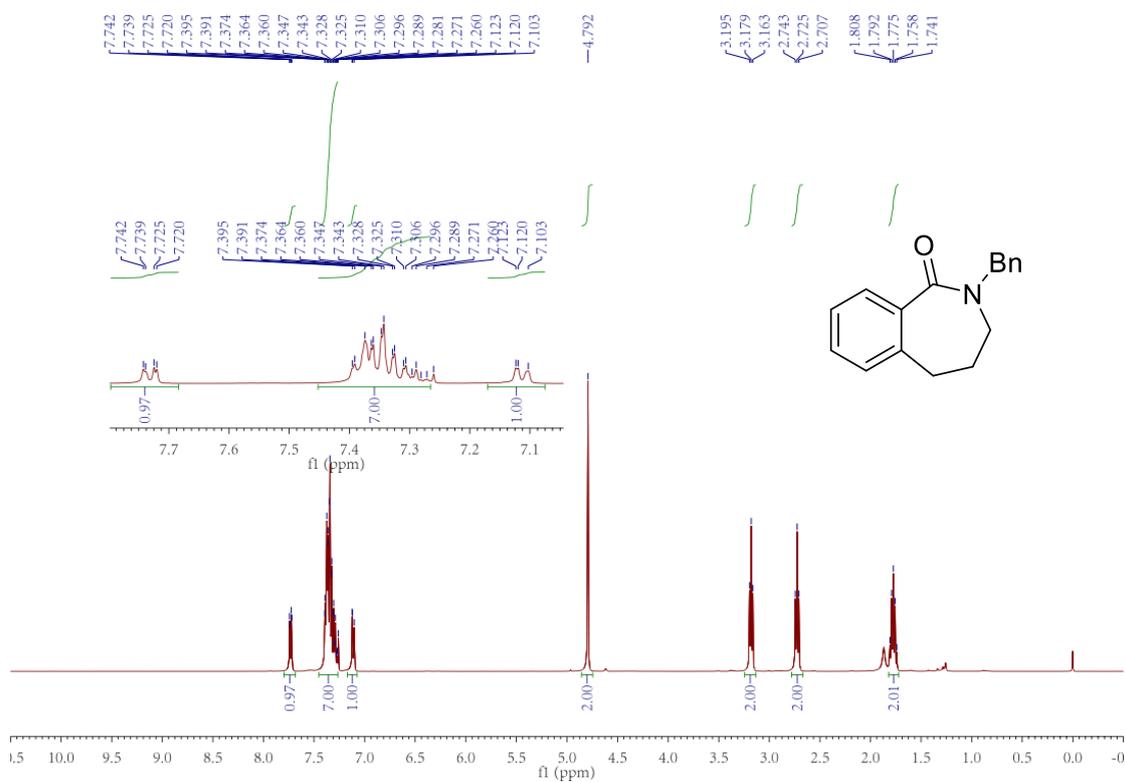


$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

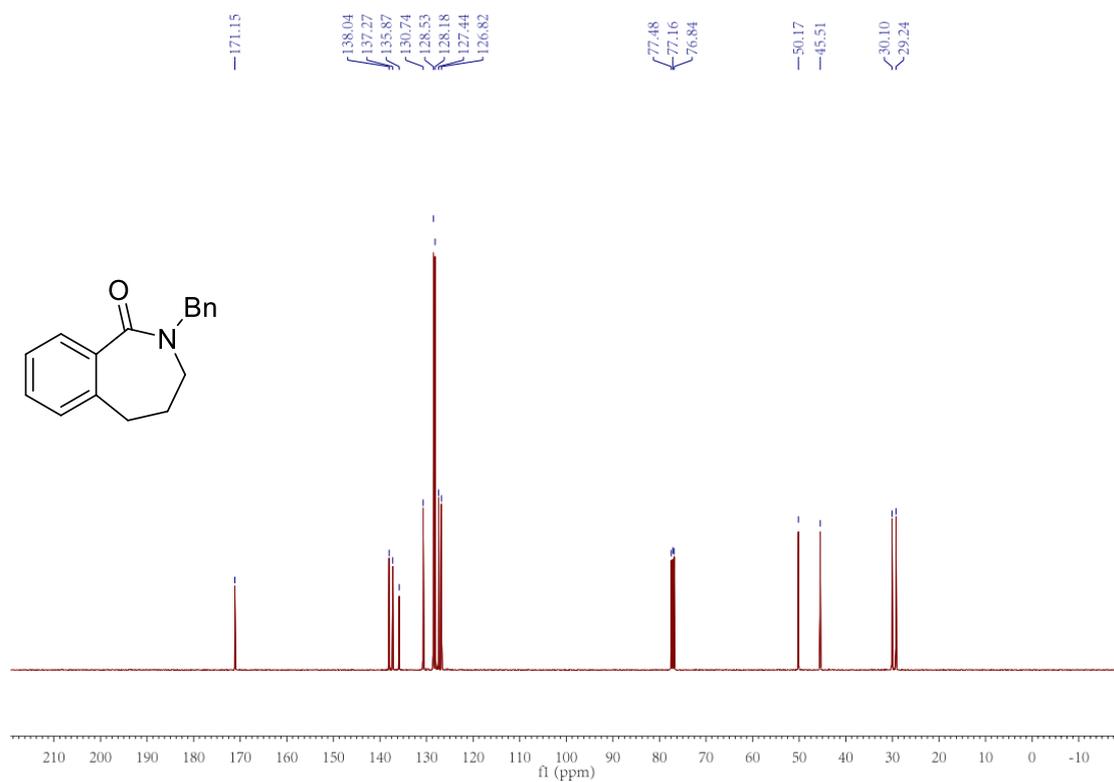


# N-Benzyltetrahydrobenzoazepin-1-one (9ga)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

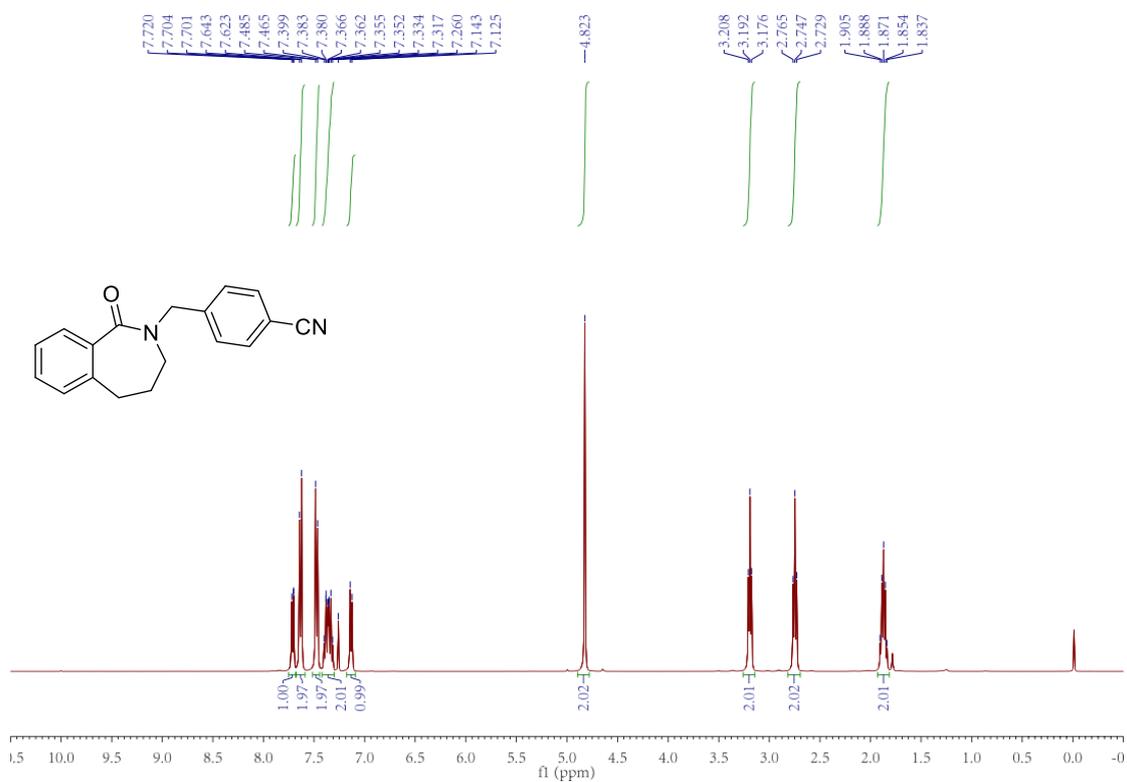


<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

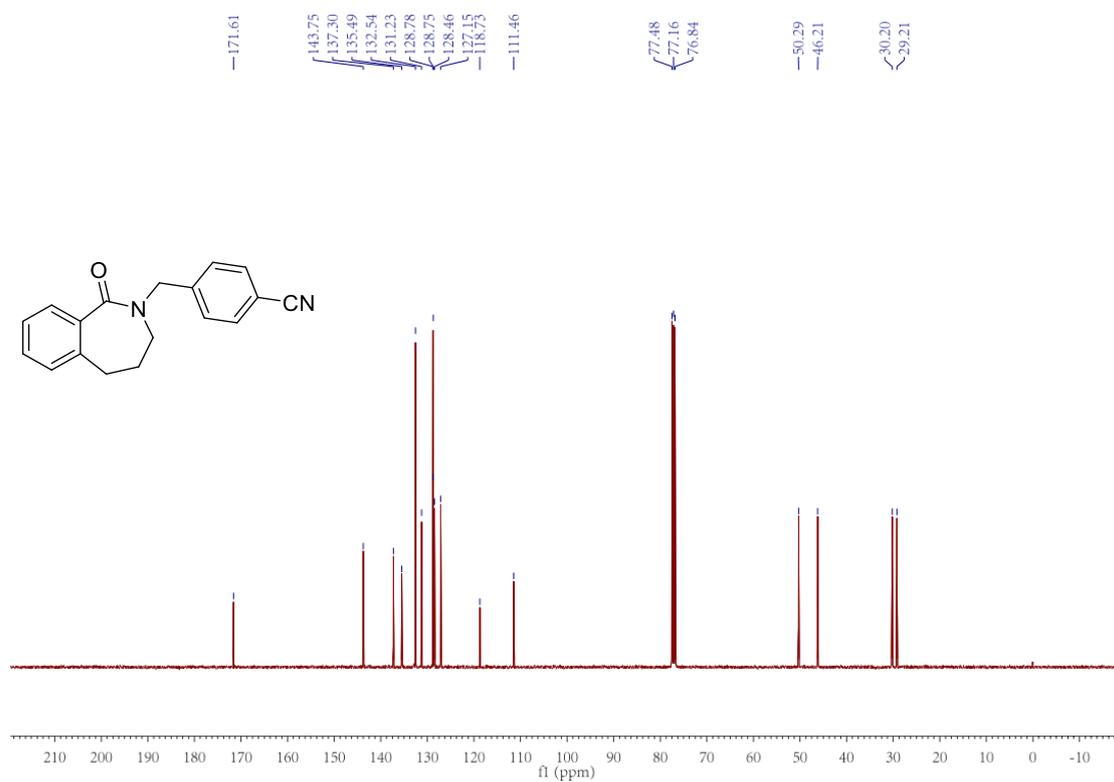


N-(4-Cyanobenzyl)tetrahydrobenzoazepin-1-one (**9ha**)

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )

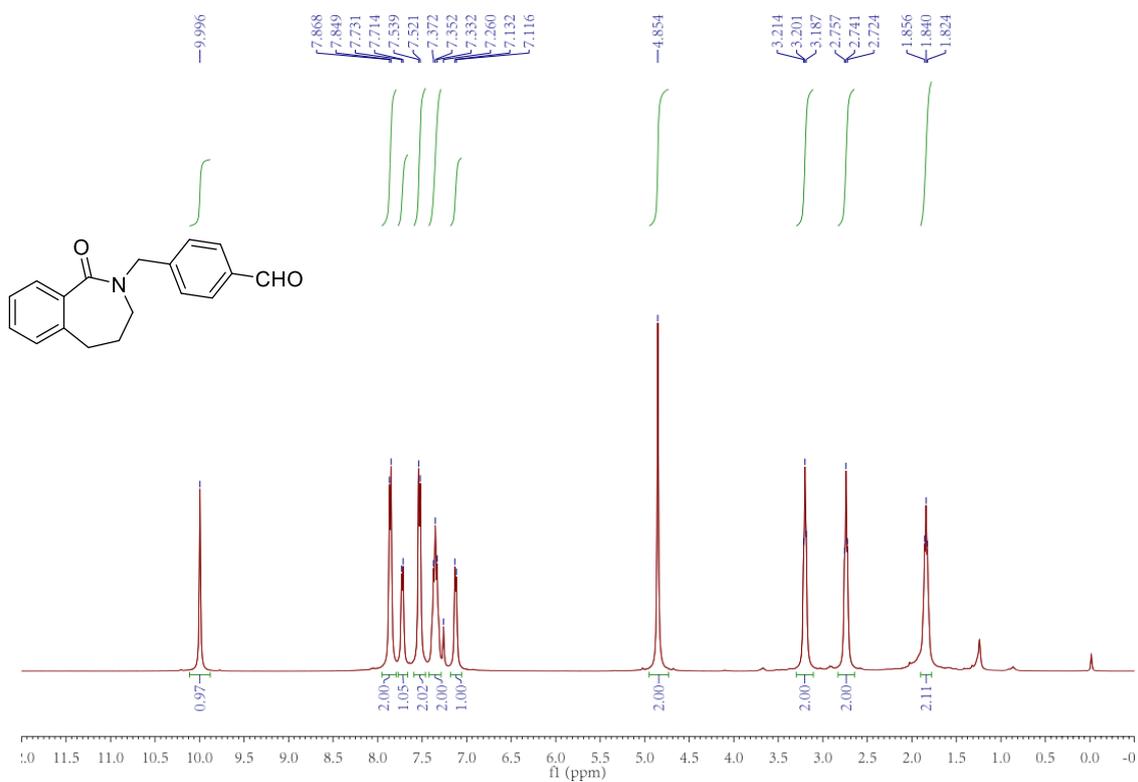


$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

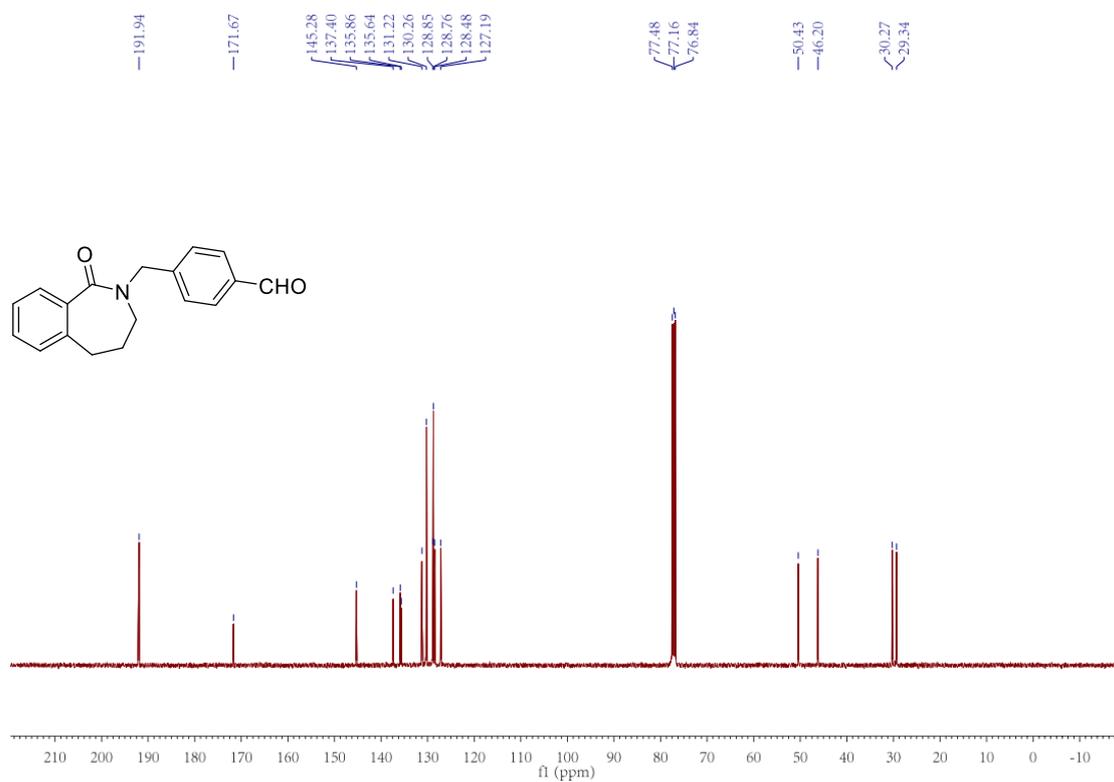


N-(4-Formylbenzyl)tetrahydrobenzoazepin-1-one (**9ia**)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

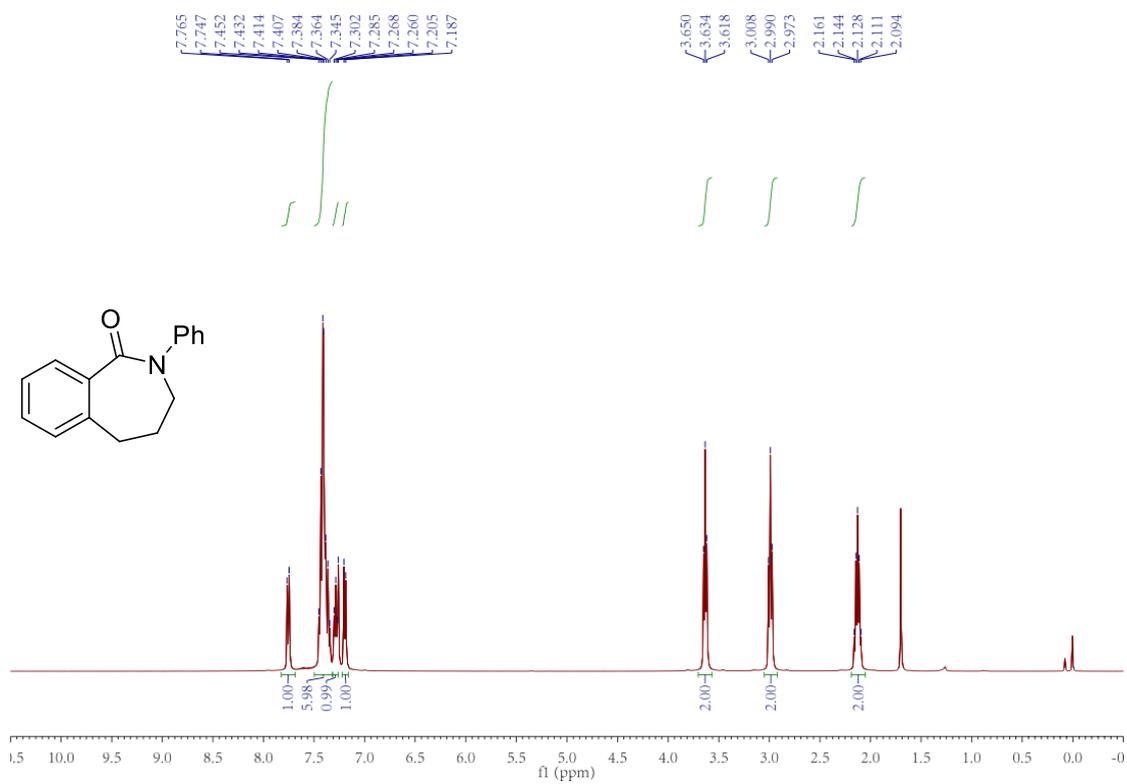


<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

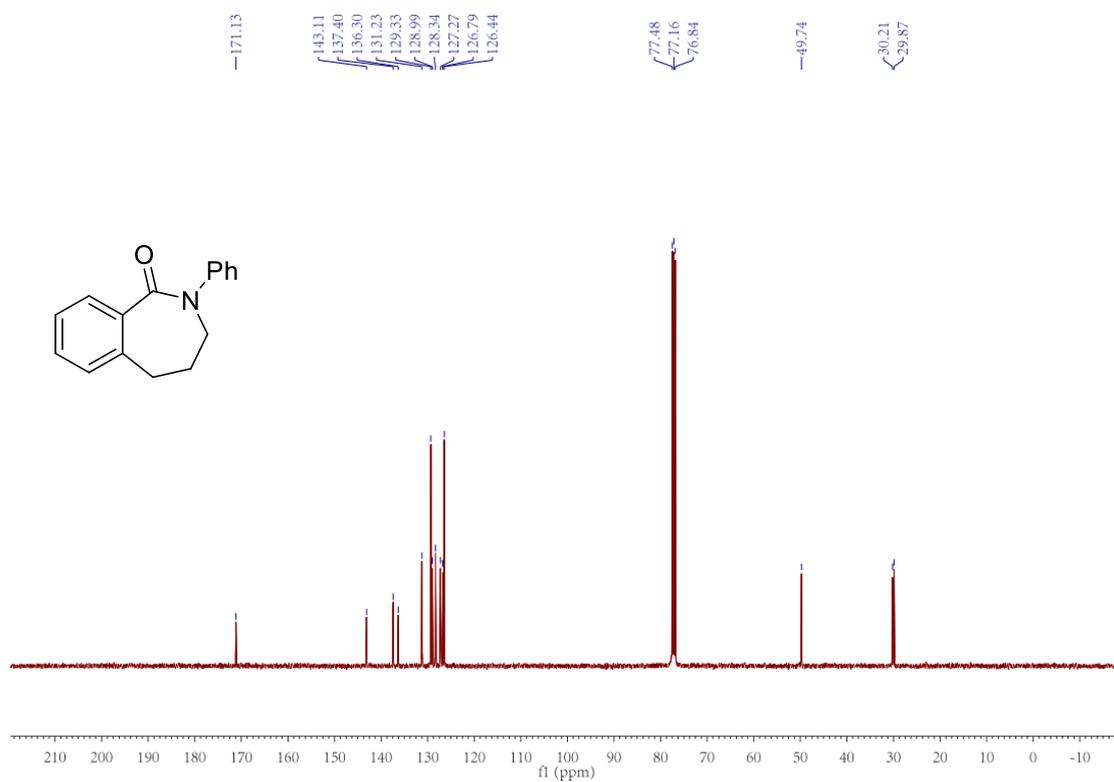


N-Phenyltetrahydrobenzoazepin-1-one (**9ja**)

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )

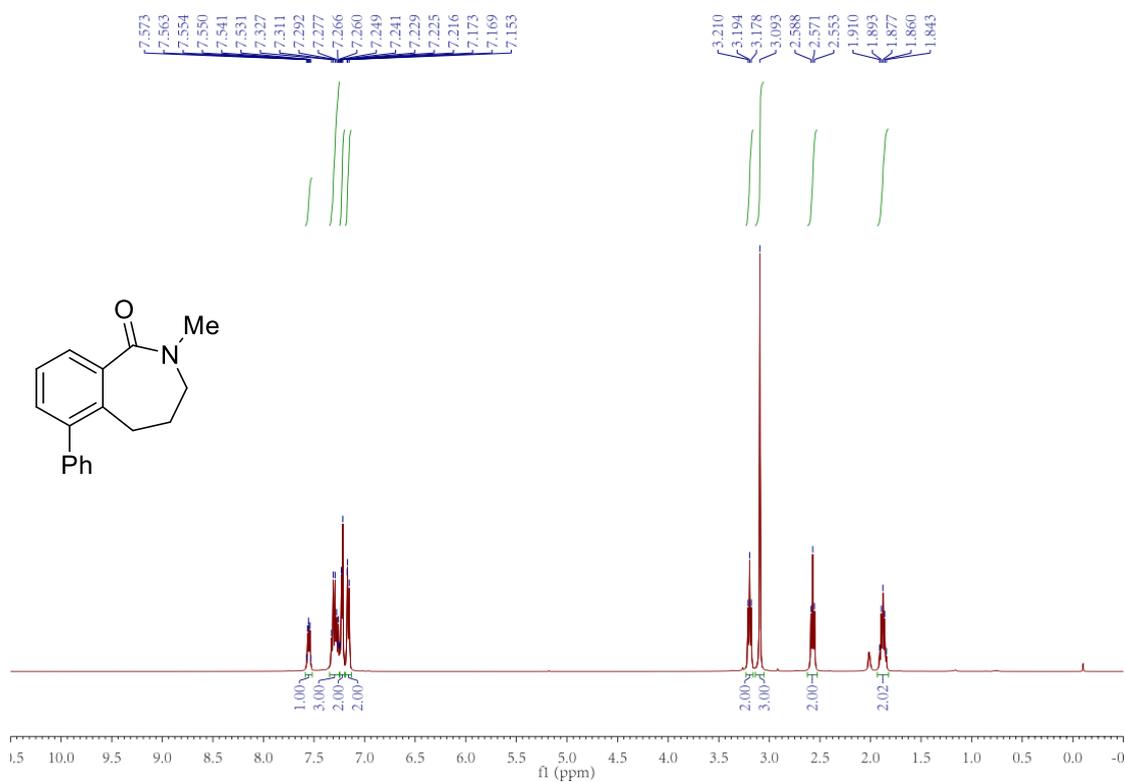


$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

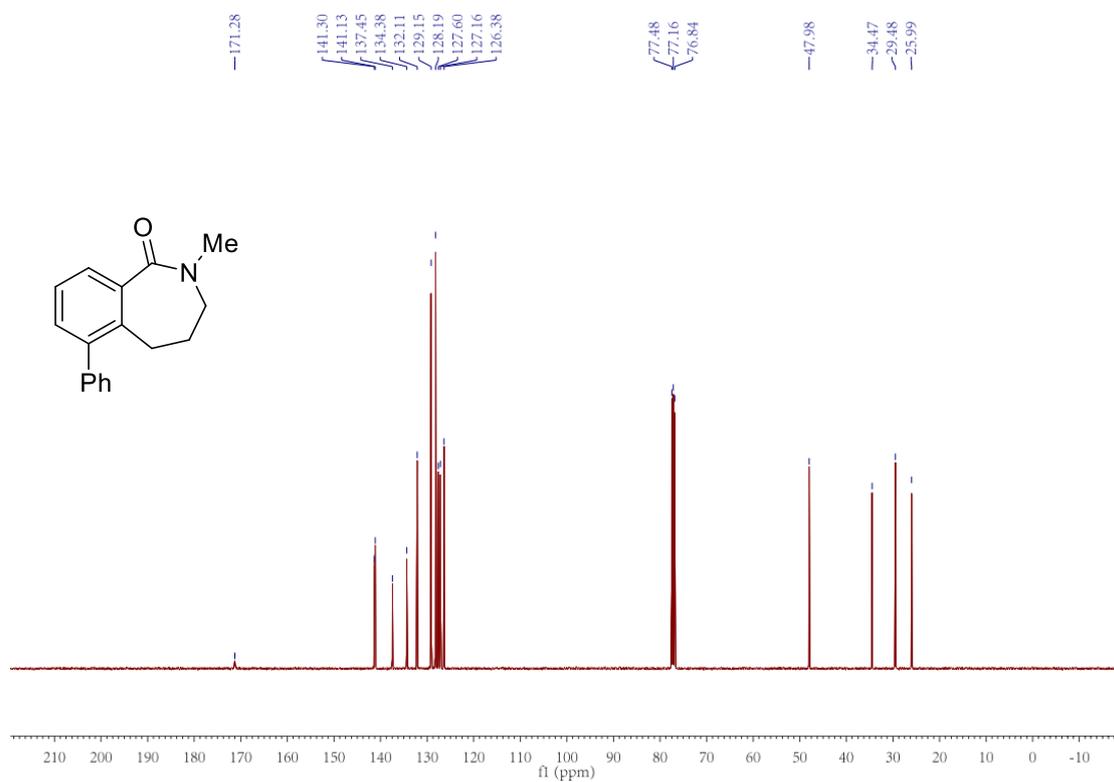


N-Methyl-6-phenyltetrahydrobenzoazepin-1-one (**9ka**)

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )

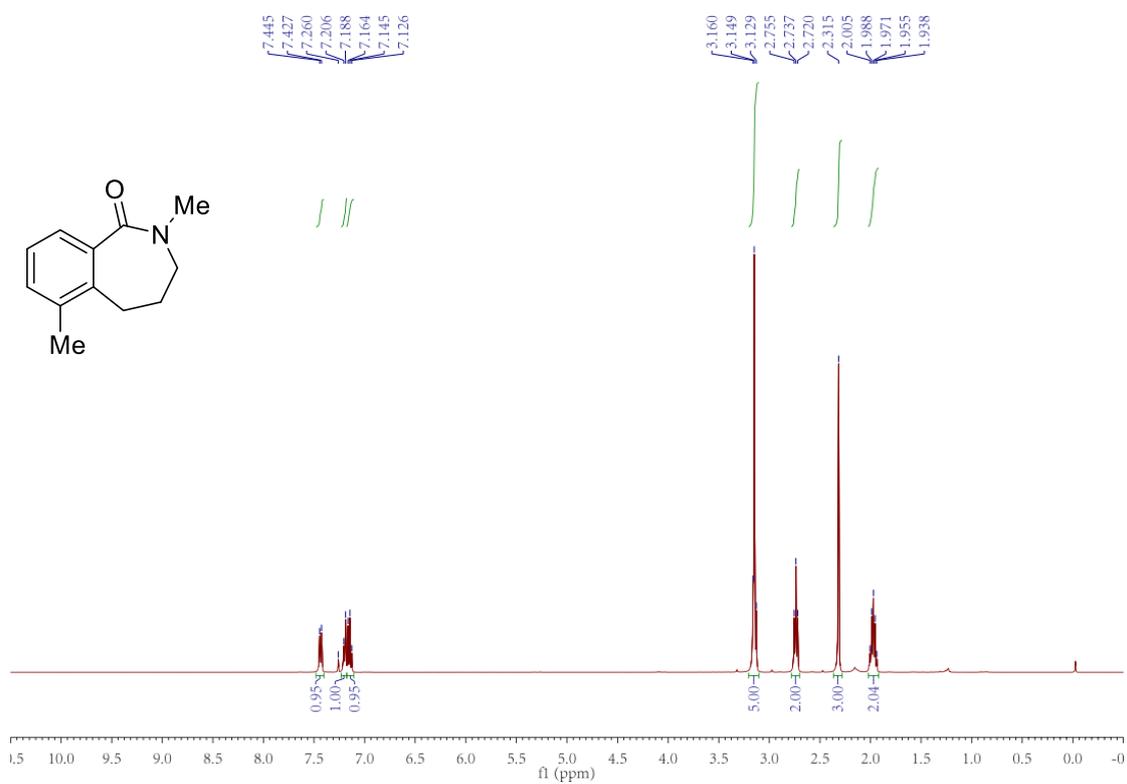


$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

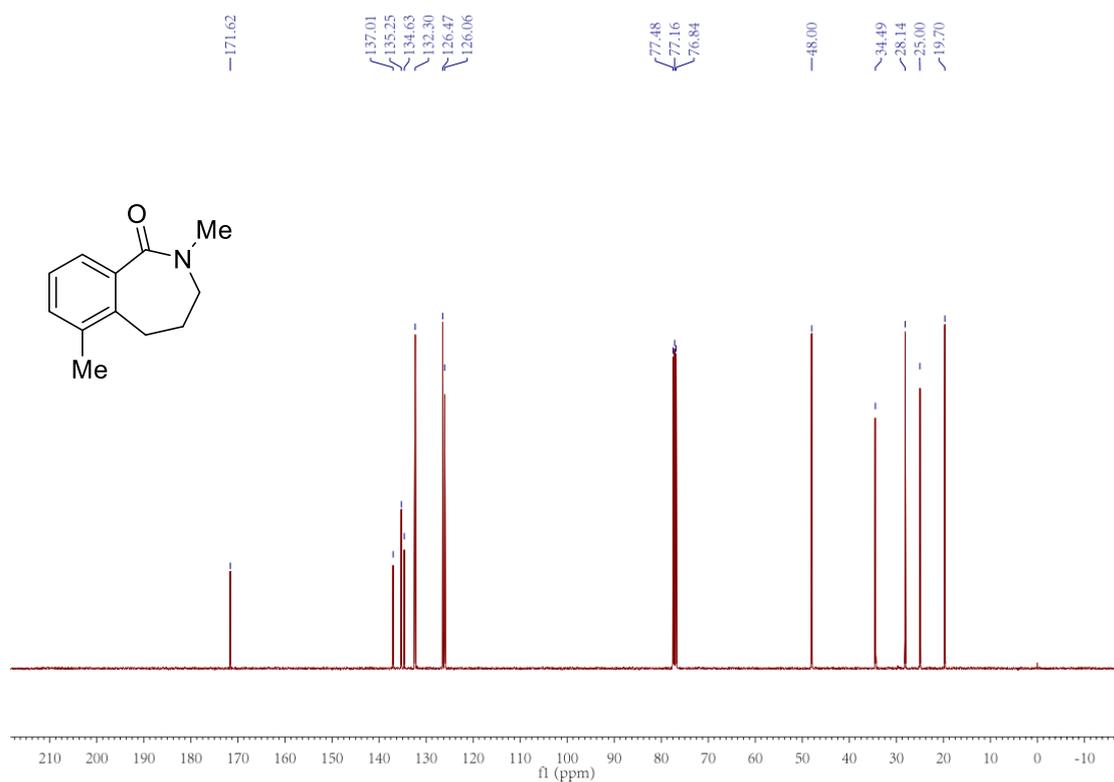


N,6-Dimethyltetrahydrobenzoozepin-1-one (**9la**)

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )

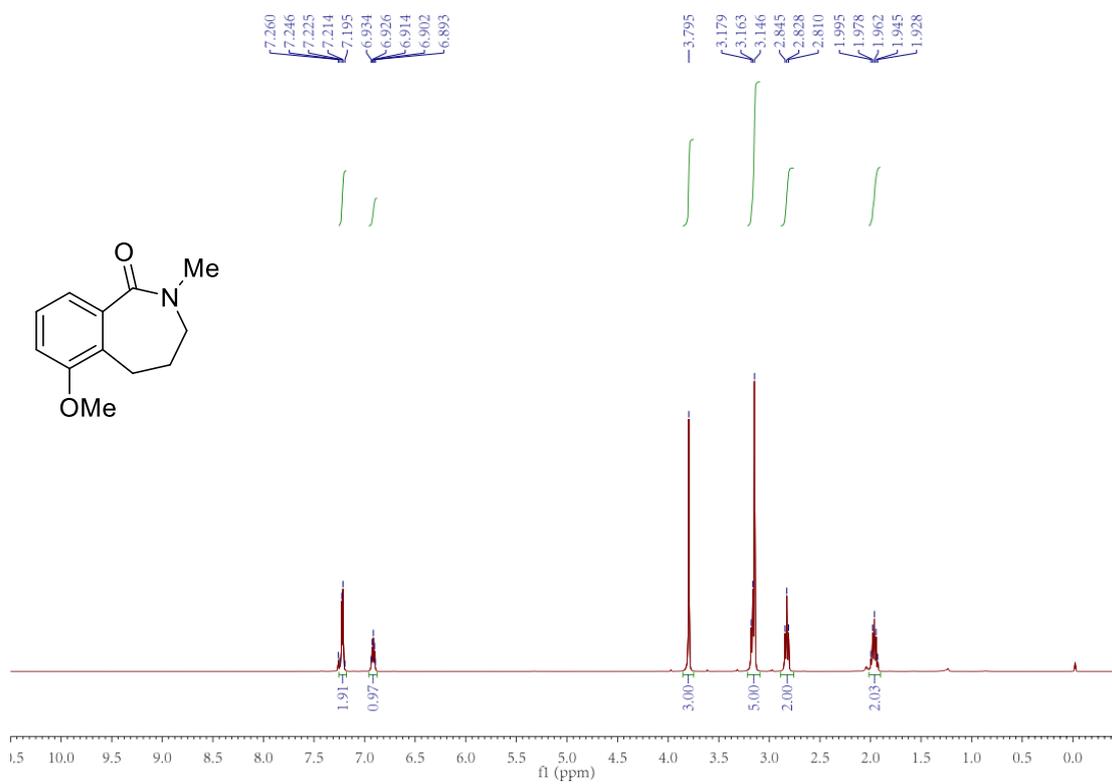


$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

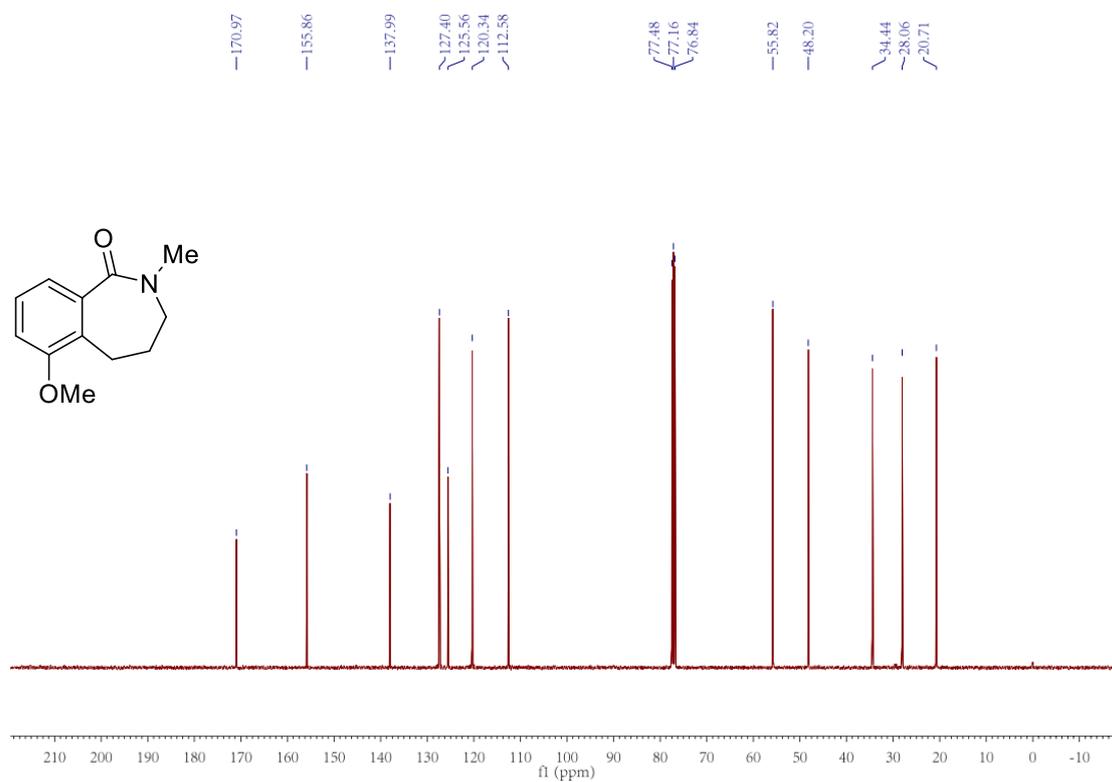


N-Methyl-6-methoxytetrahydrobenzoazepin-1-one (**9ma**)

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )

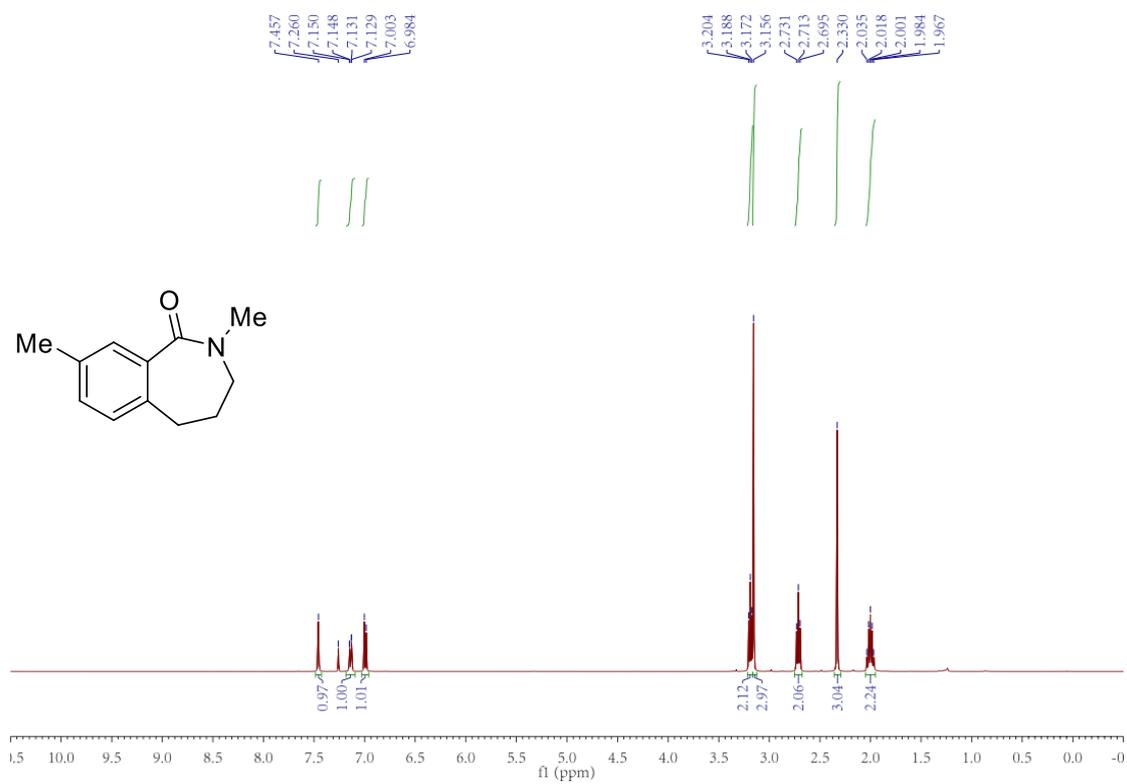


$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

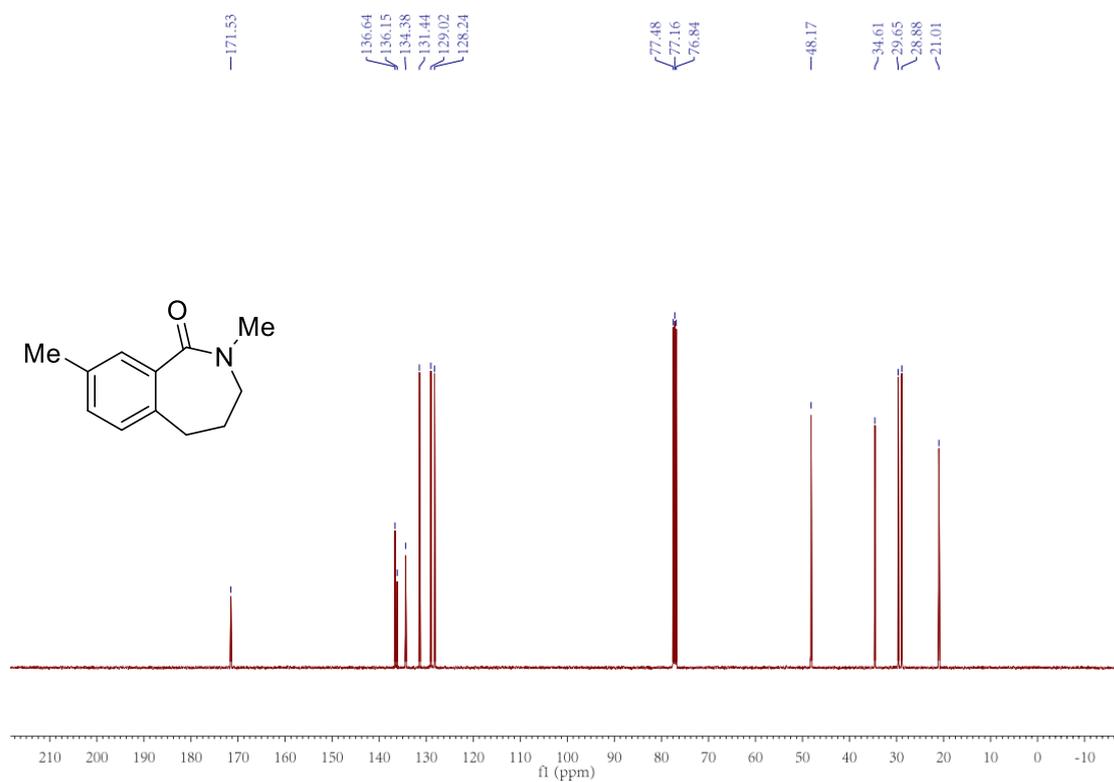


N,8-Dimethyltetrahydrobenzoazepin-1-one (**9na**)

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )

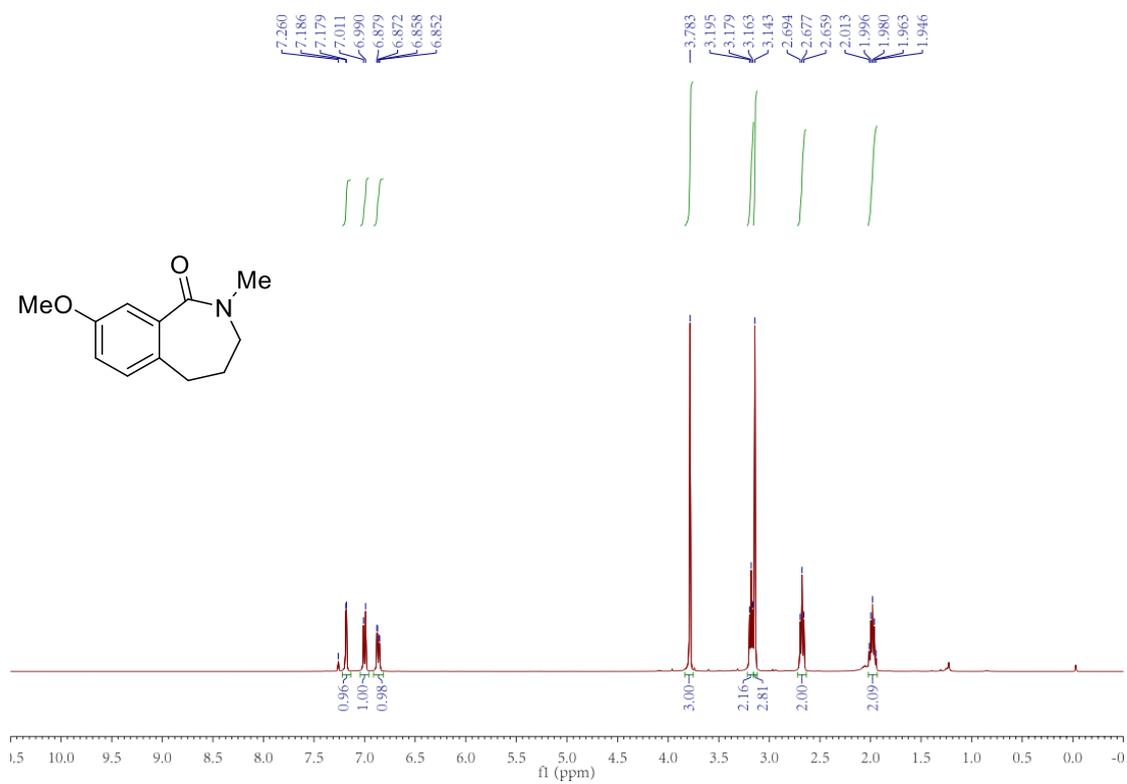


$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

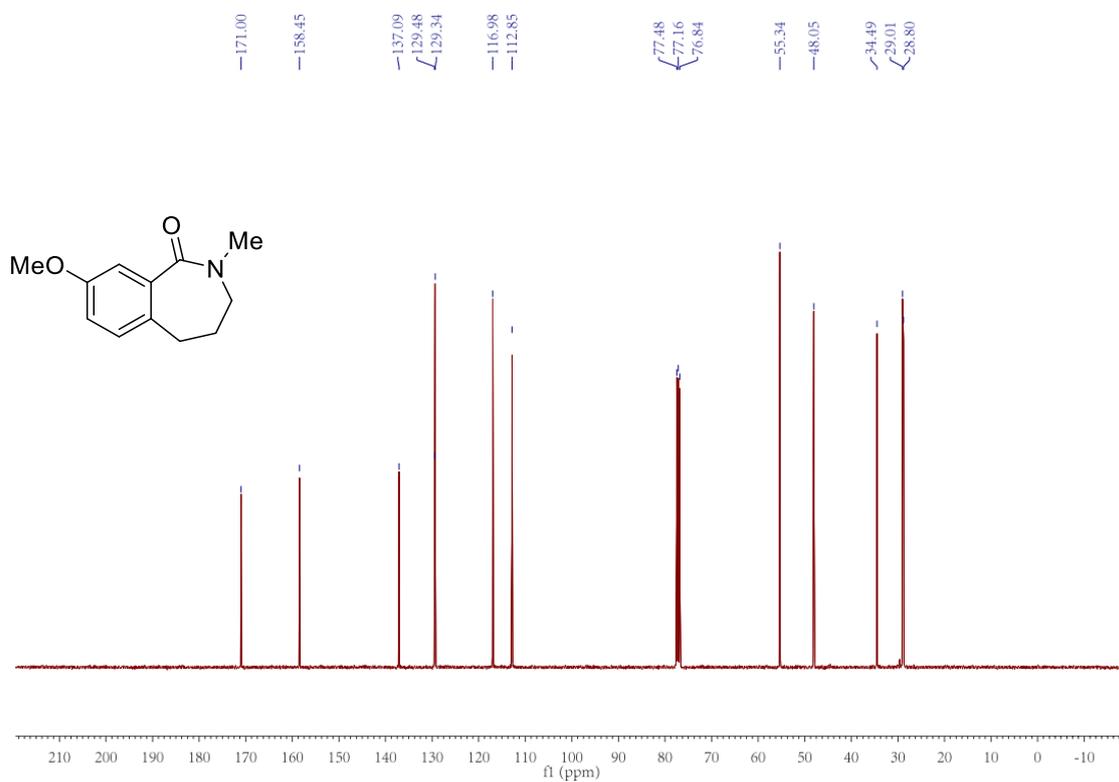


N-Methyl-8-methoxytetrahydrobenzoazepin-1-one (**9oa**)

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )

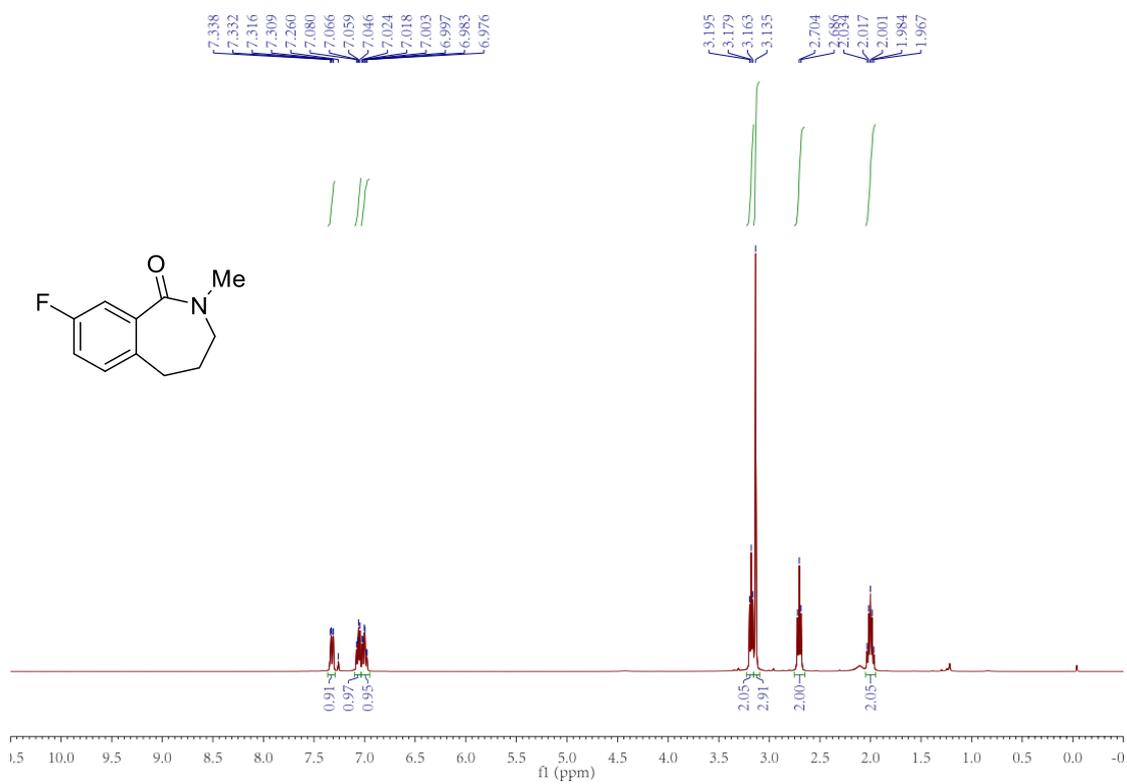


$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

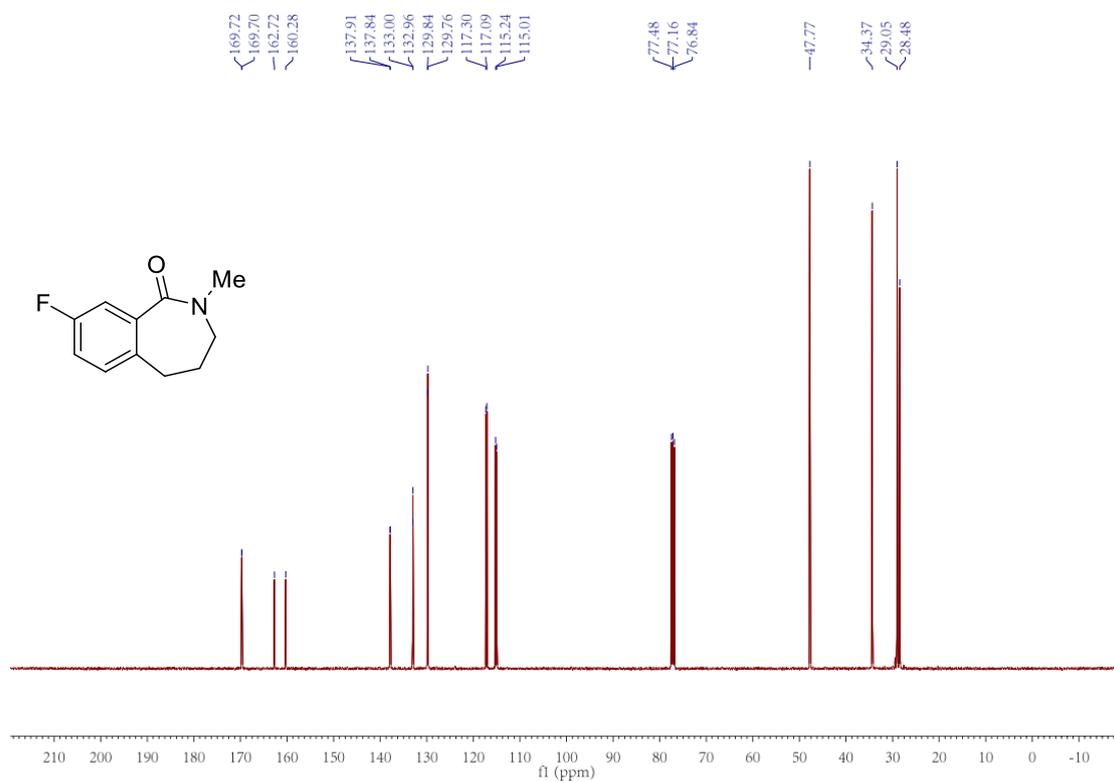


N-Methyl-8-fluorotetrahydrobenzoazepin-1-one (**9pa**)

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )

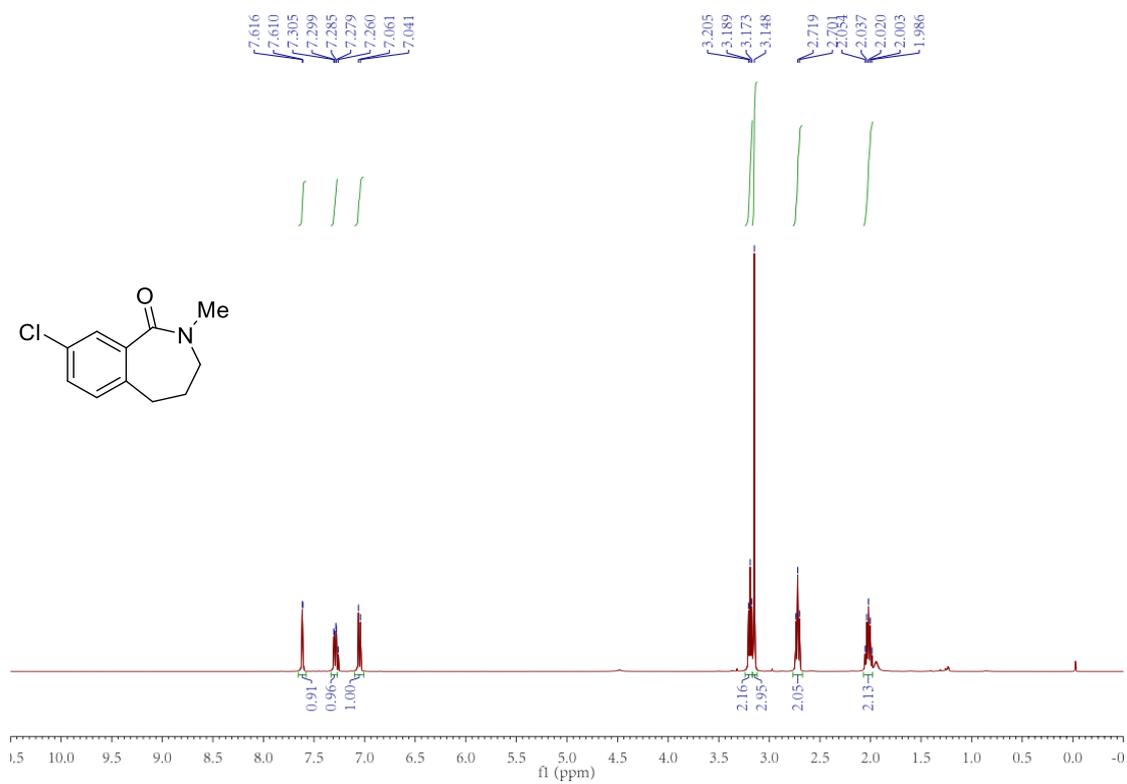


$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

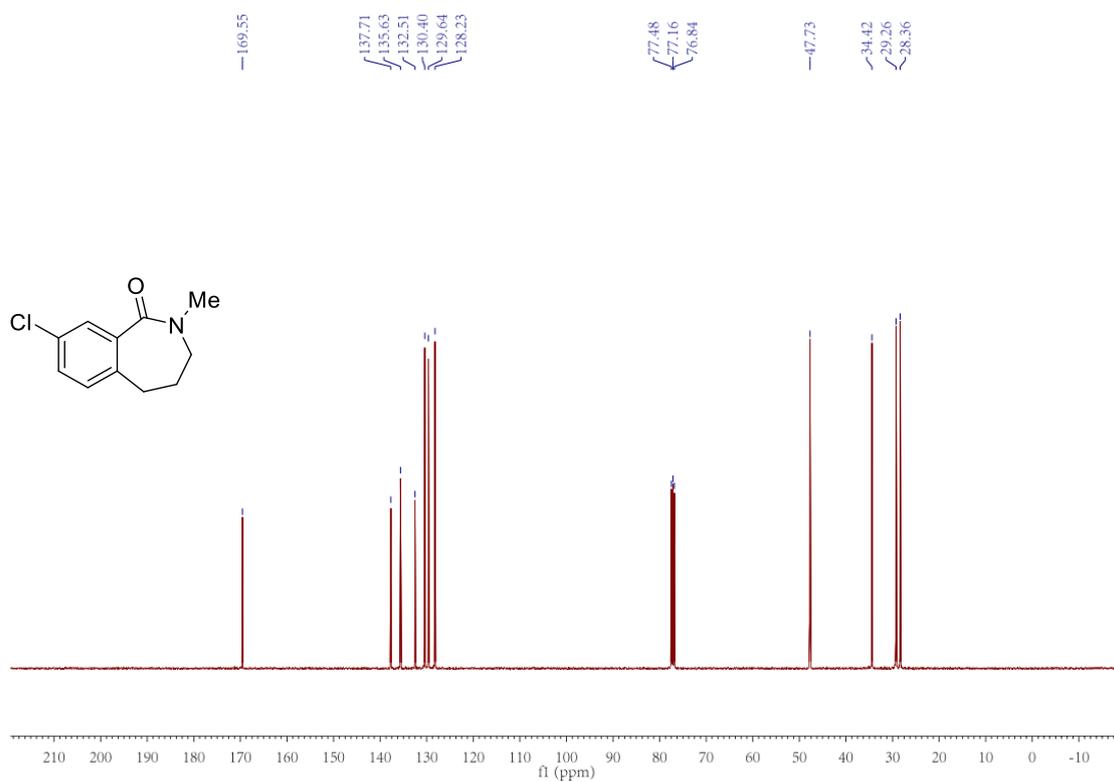


N-Methyl-8-chlorotetrahydrobenzoozepin-1-one (**9qa**)

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )

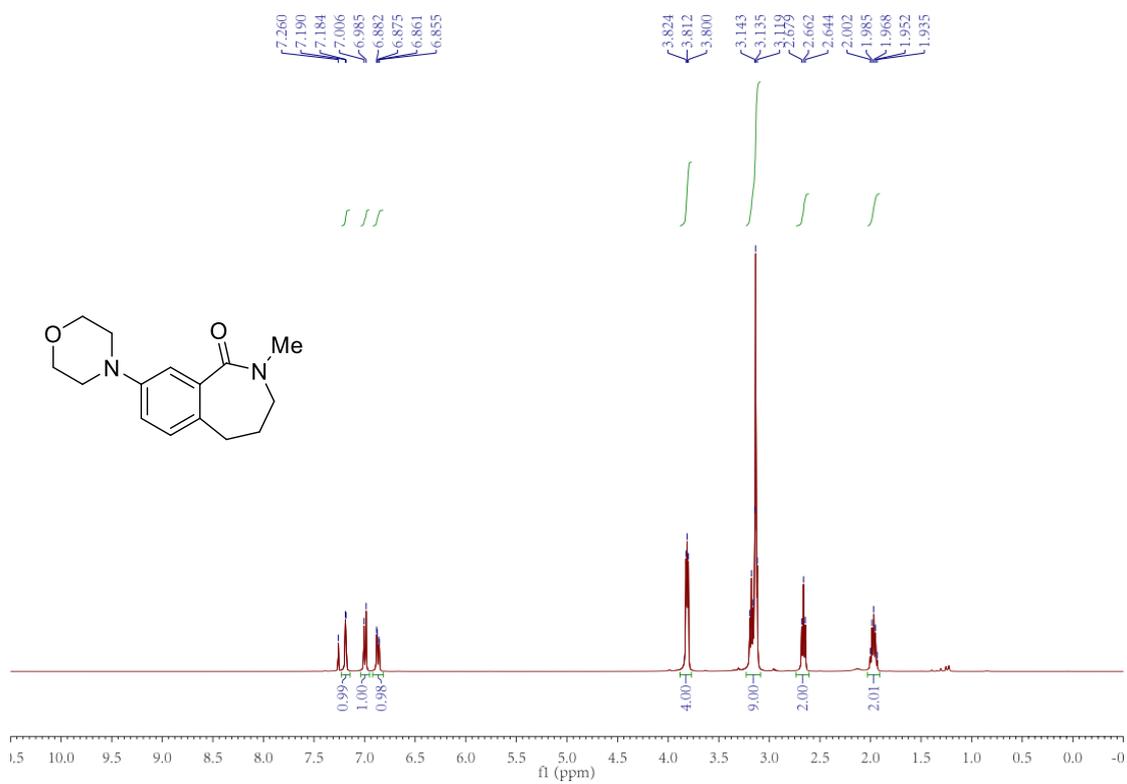


$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

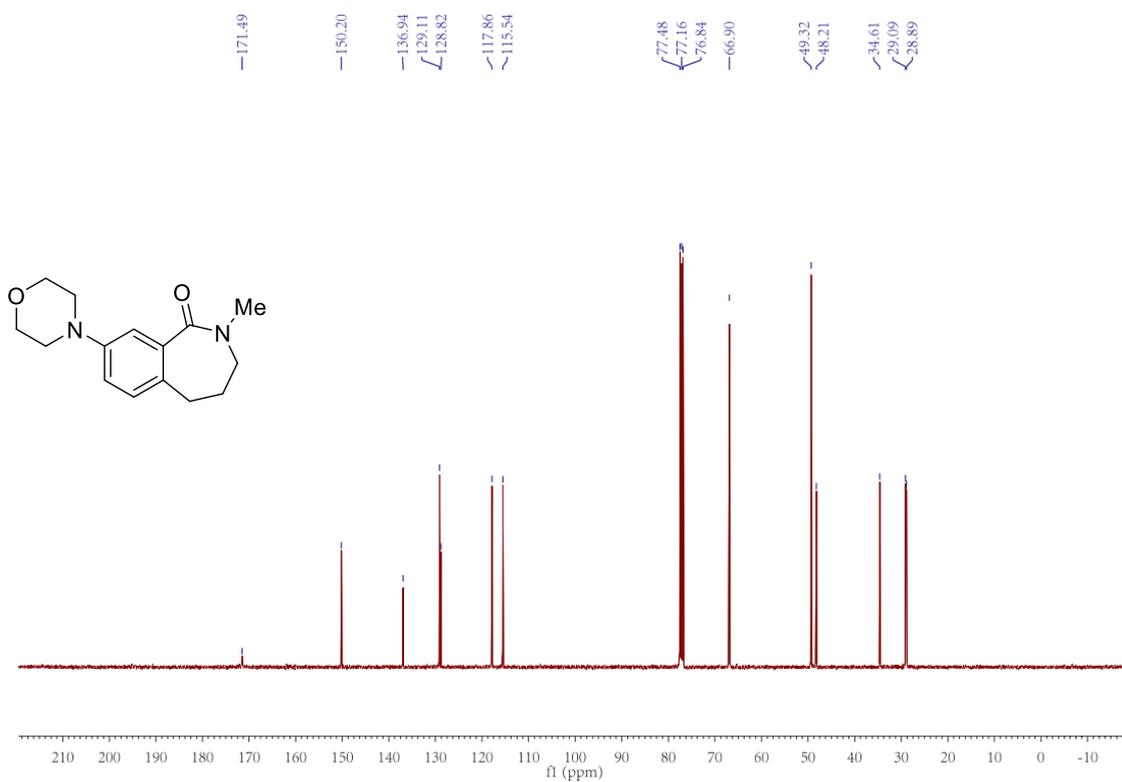


N-Methyl-8-morpholinotetrahydrobenzoazepin-1-one (**9ra**)

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )

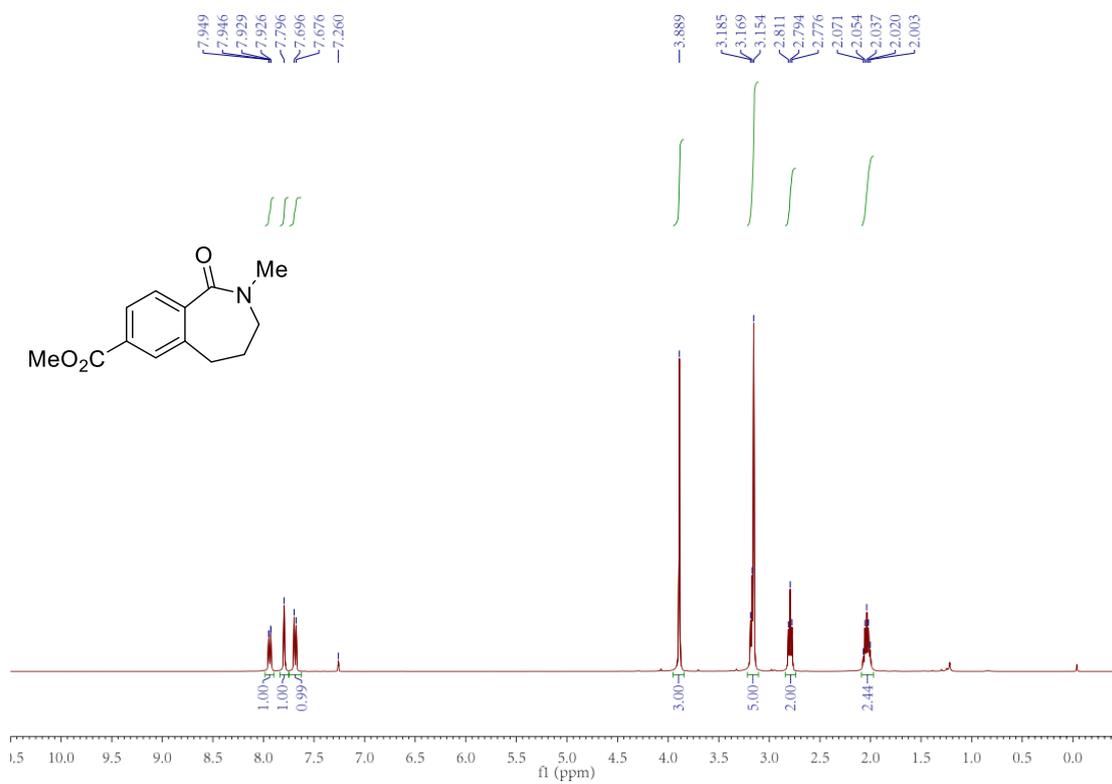


$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

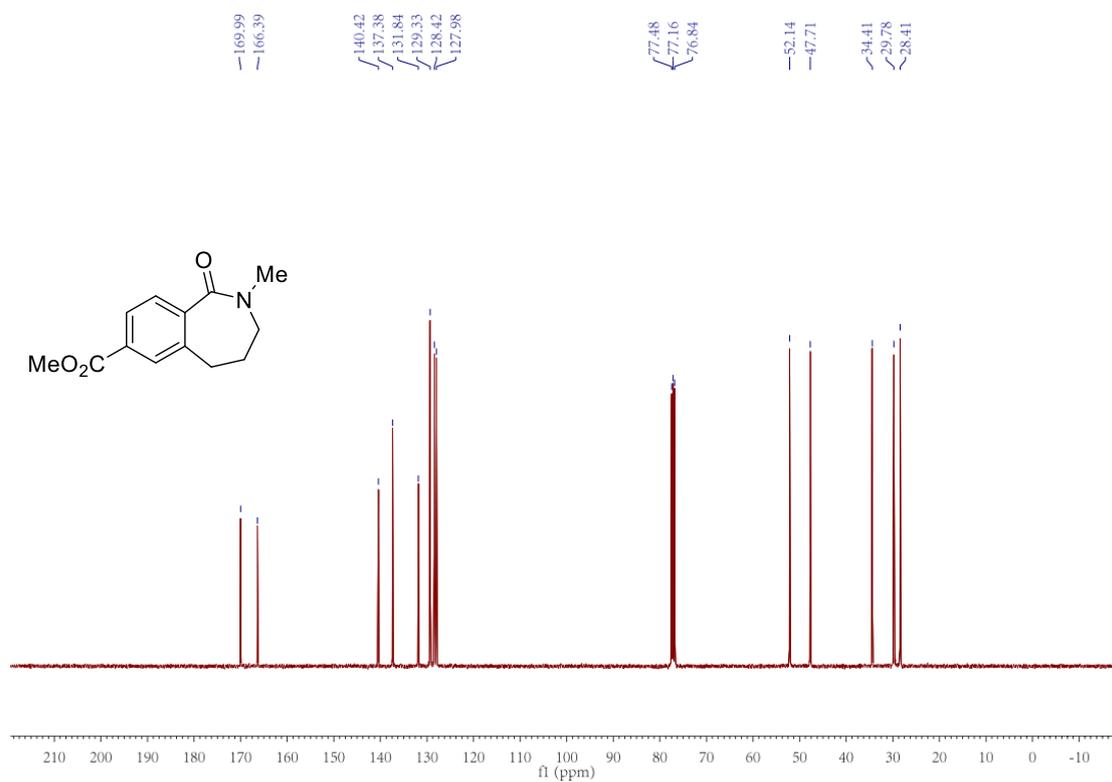


N-Methyl-7-(methoxycarbonyl)tetrahydrobenzoazepin-1-one (**9sa**)

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )

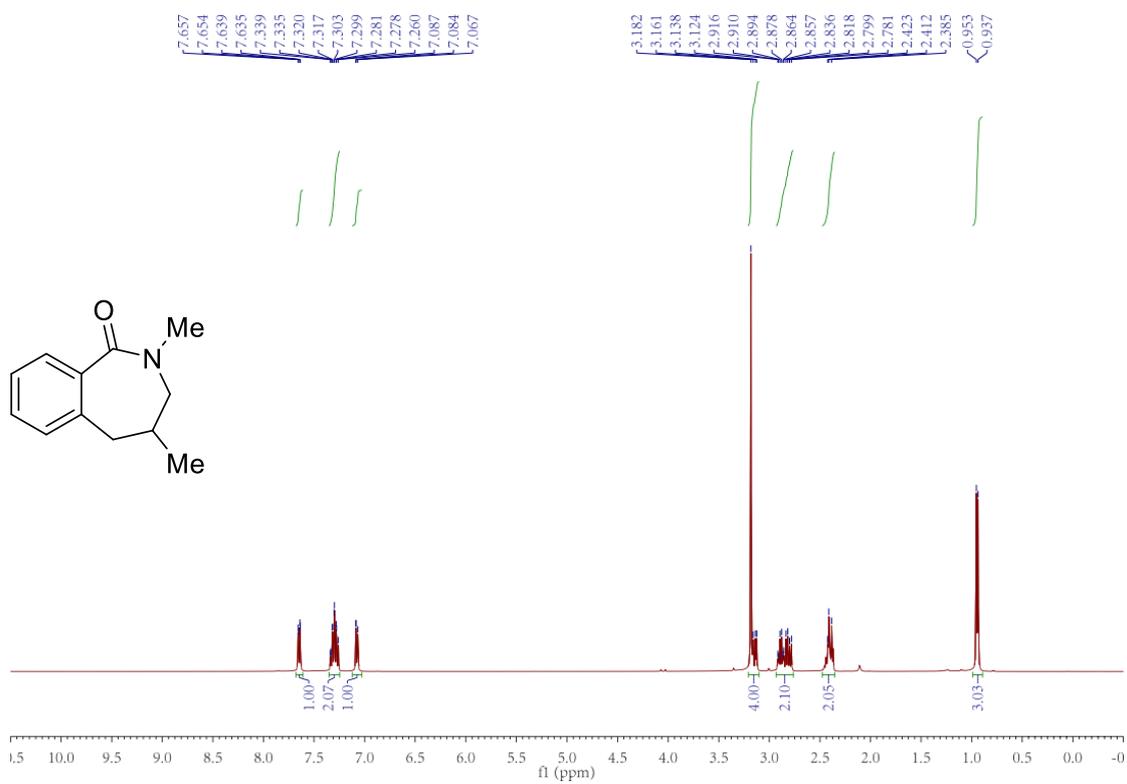


$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

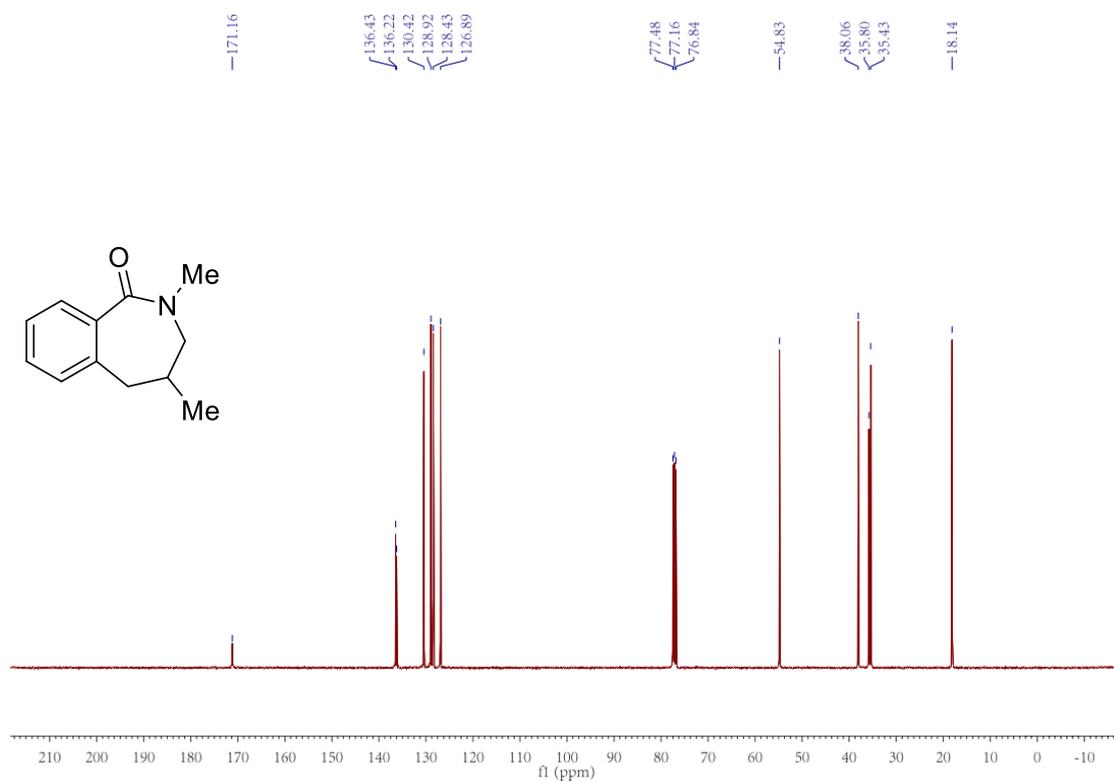


N,4-Dimethyltetrahydrobenzoazepin-1-one (**9af**)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

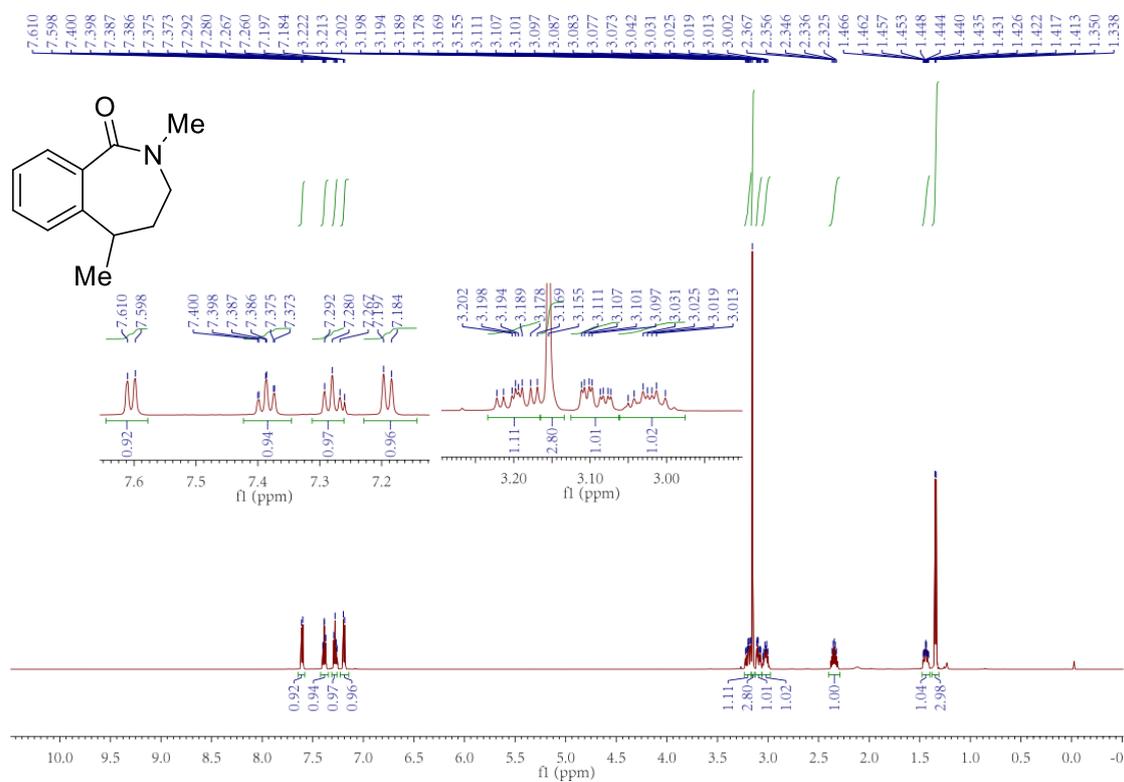


<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

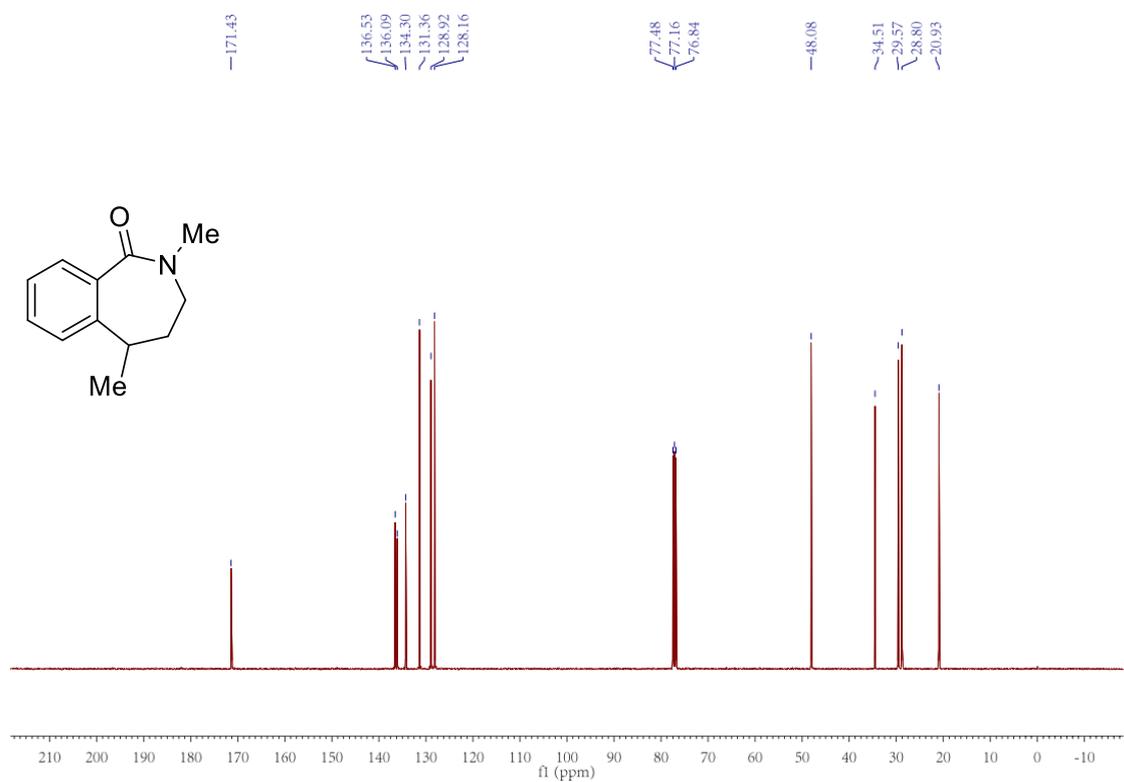


# N,5-Dimethyltetrahydrobenzoazepin-1-one (**9ag**)

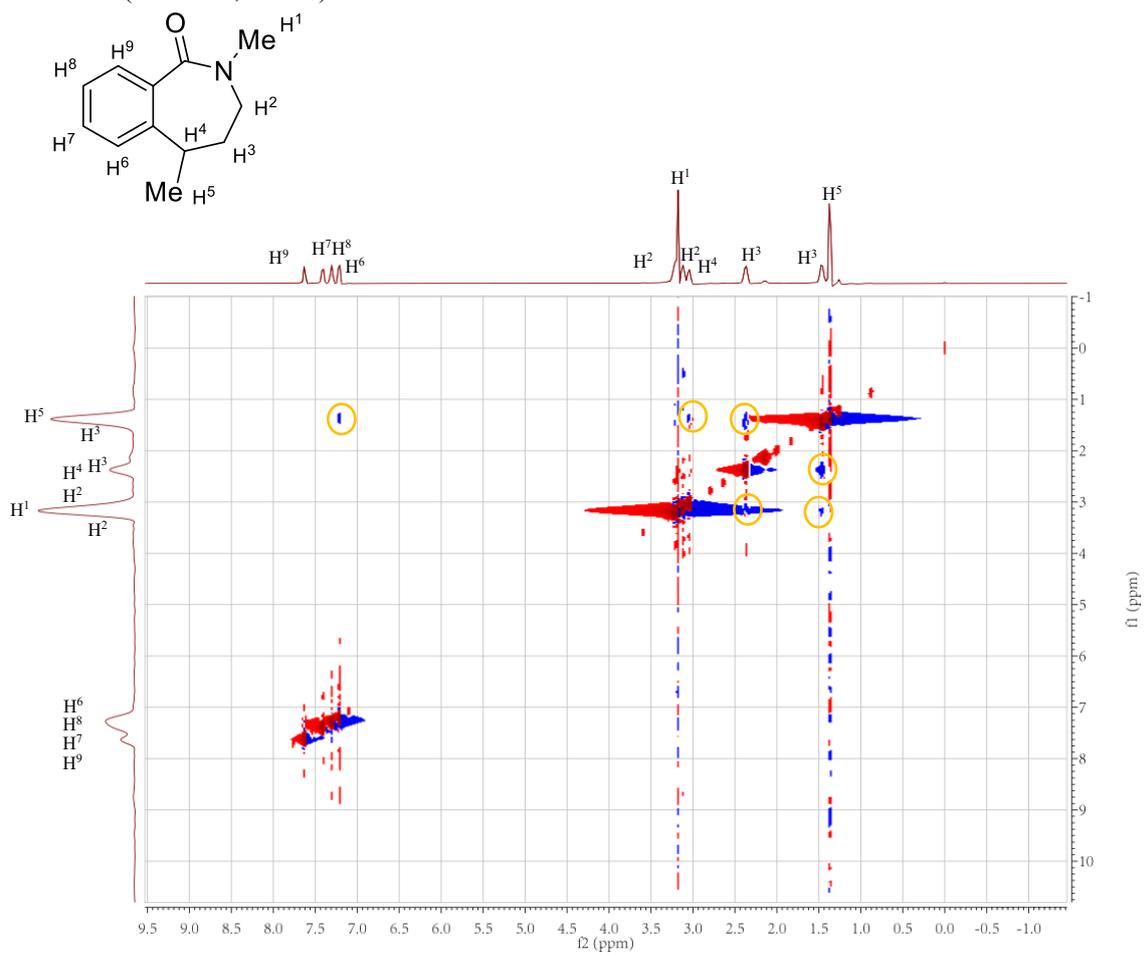
<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)



<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

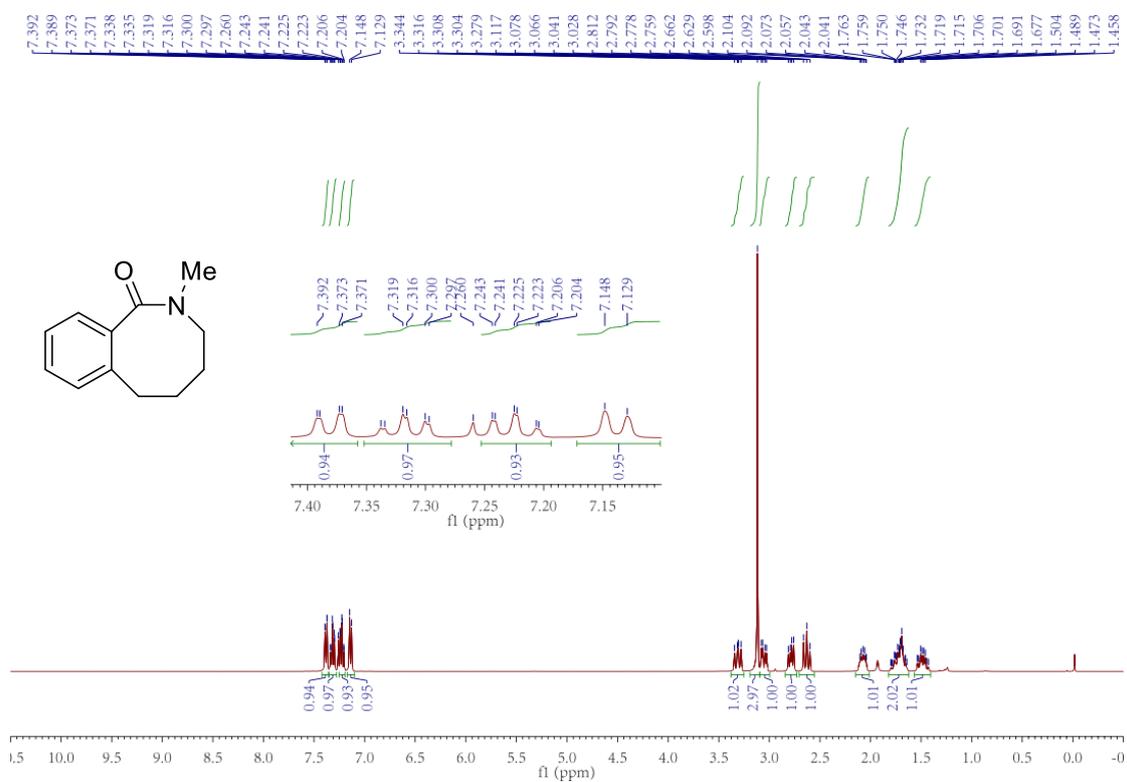


NOESY (600 MHz, CDCl<sub>3</sub>)

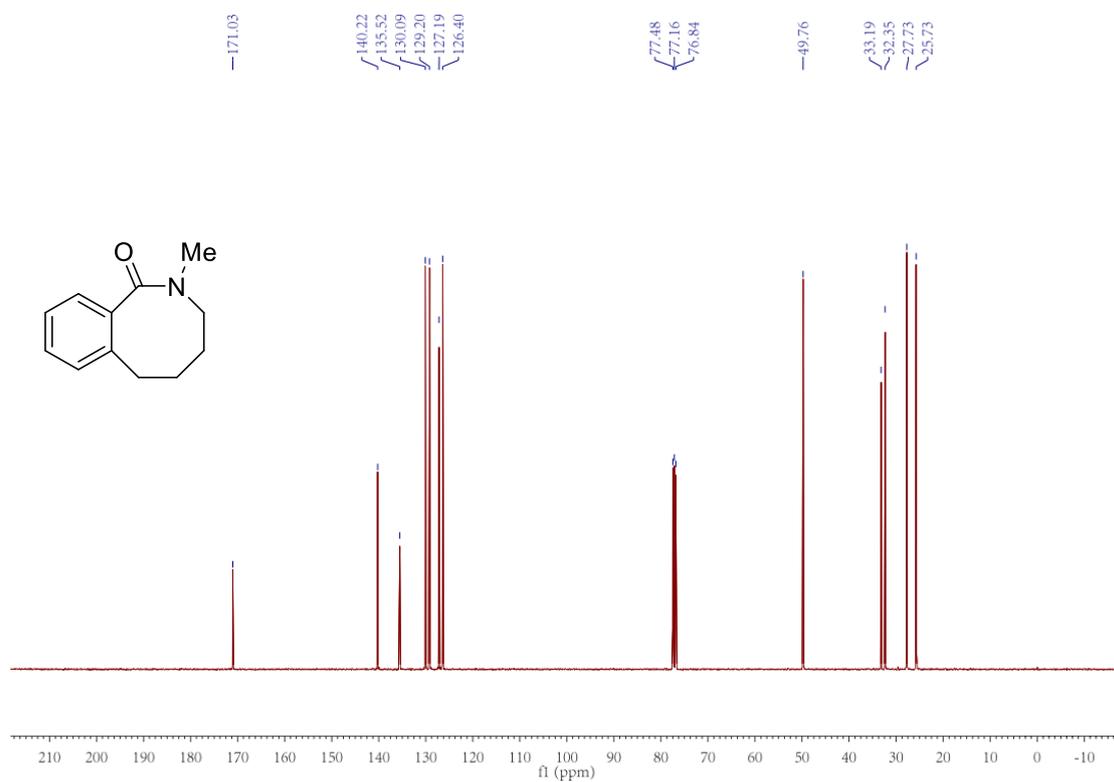


# N-Methyltetrahydrobenzoazocin-1(2H)-one (10aa)

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )

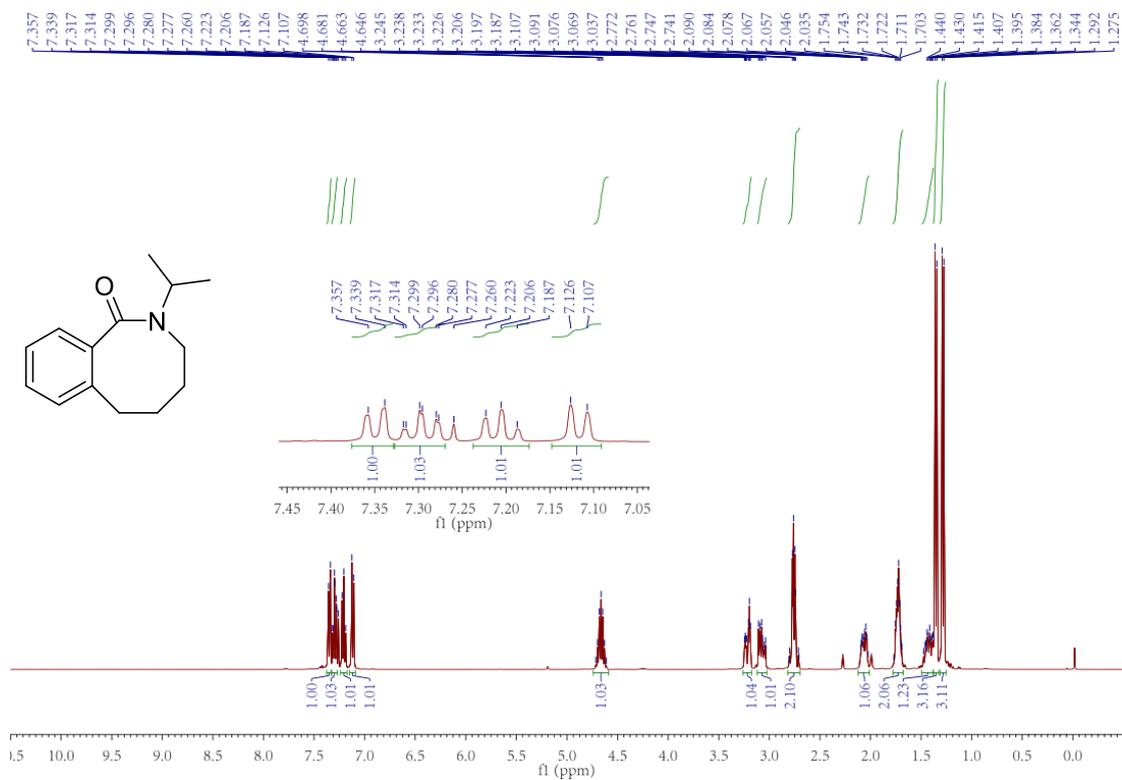


$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

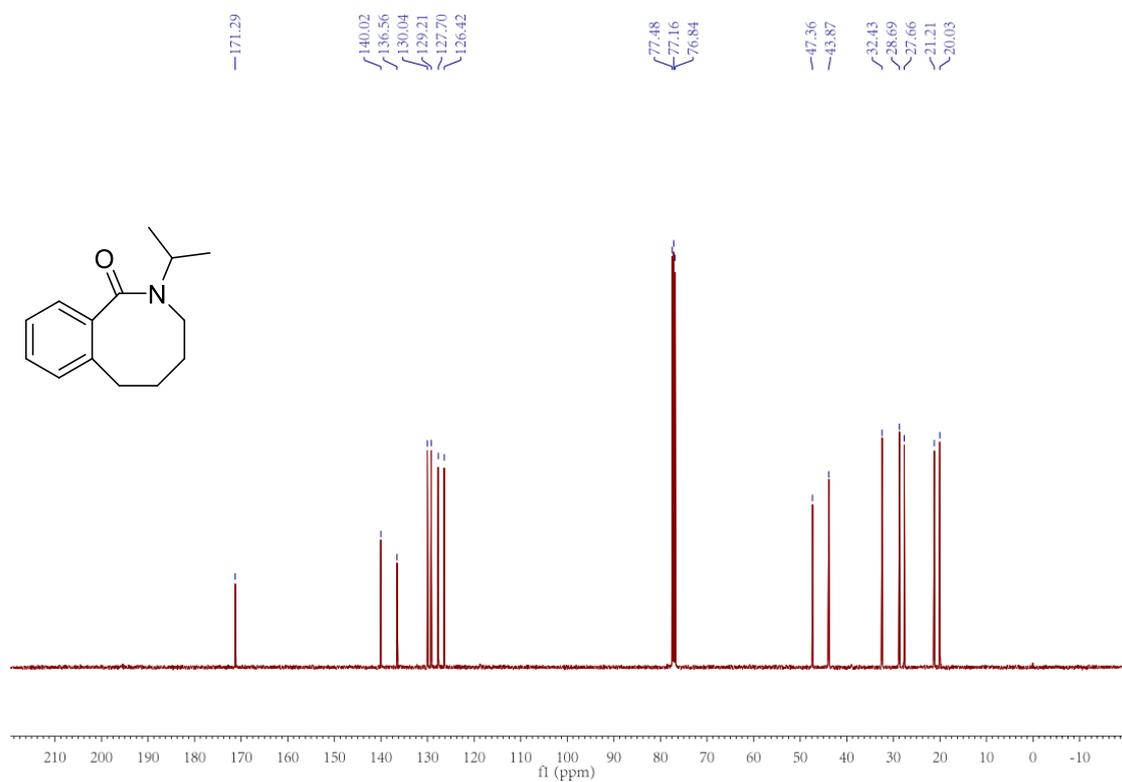


# N-Isopropyltetrahydrobenzoazocin-1(2H)-one (10ca)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

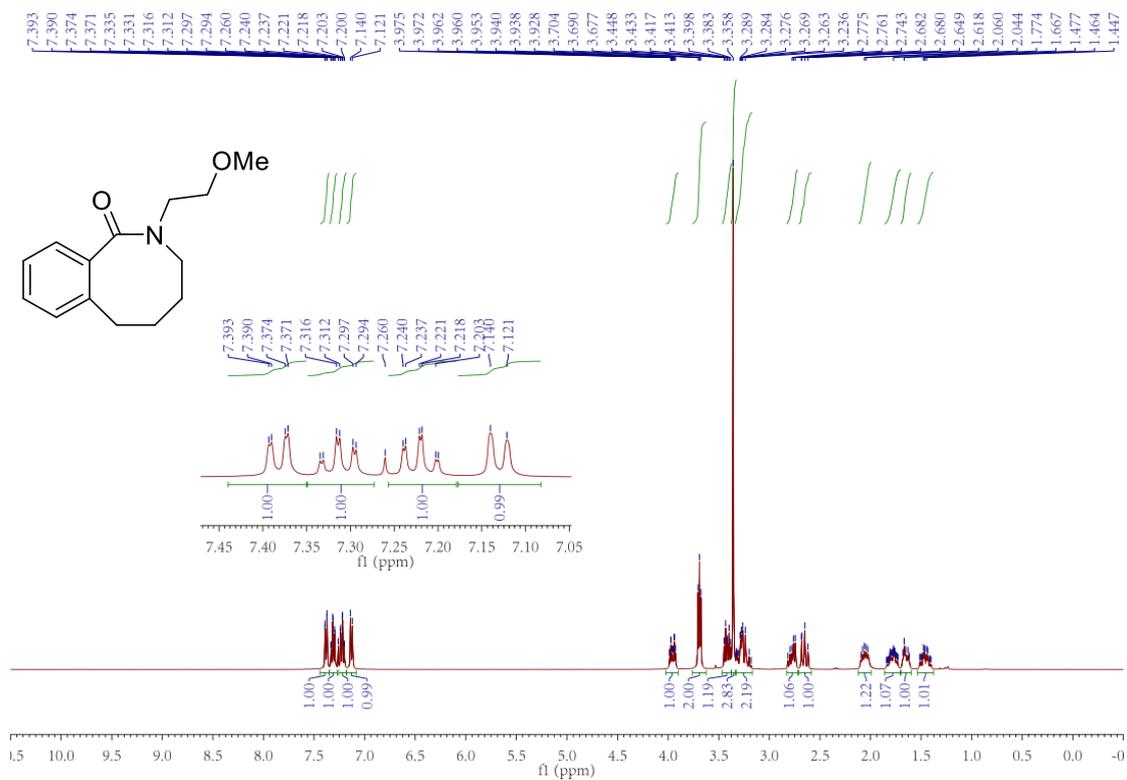


<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

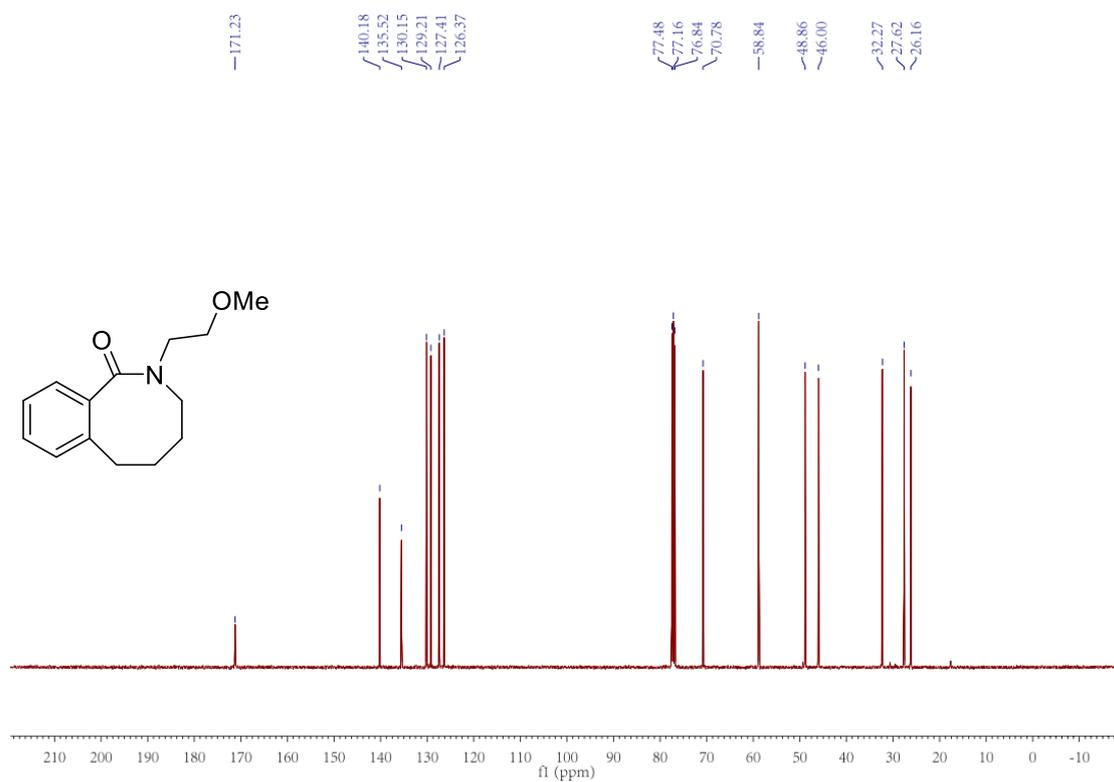


# N-(2-Methoxy)ethyltetrahydrobenzoazocin-1(2H)-one (10da)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

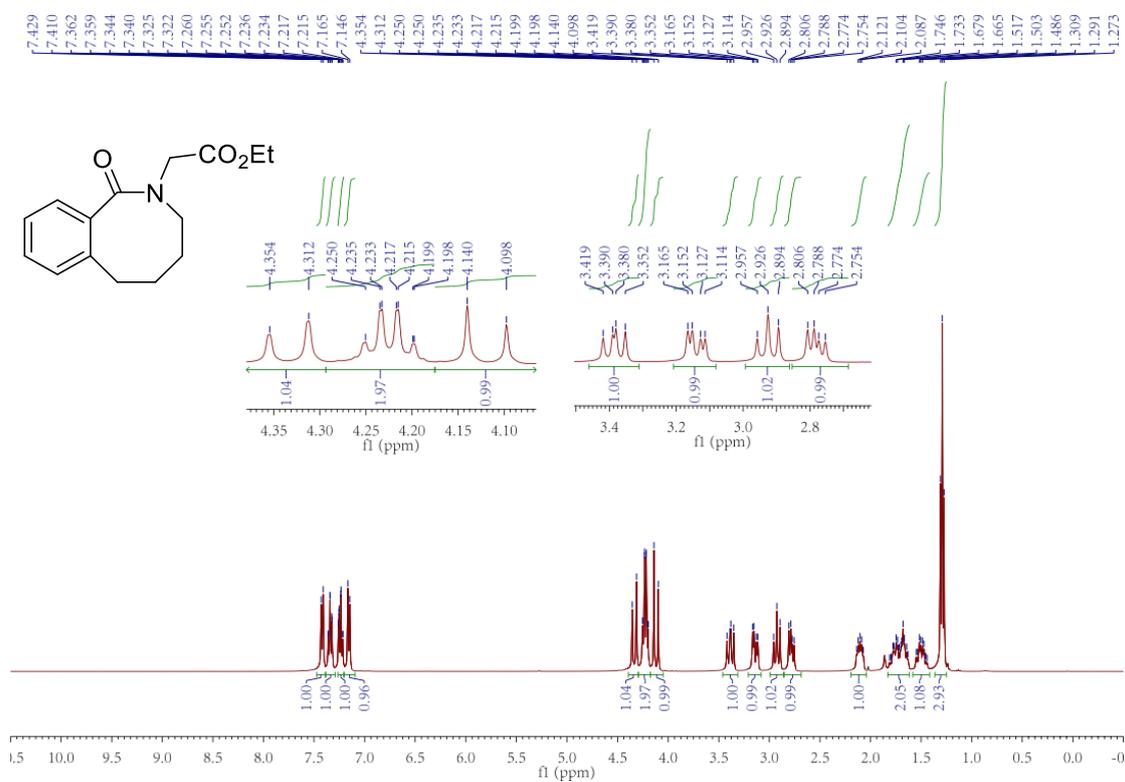


<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

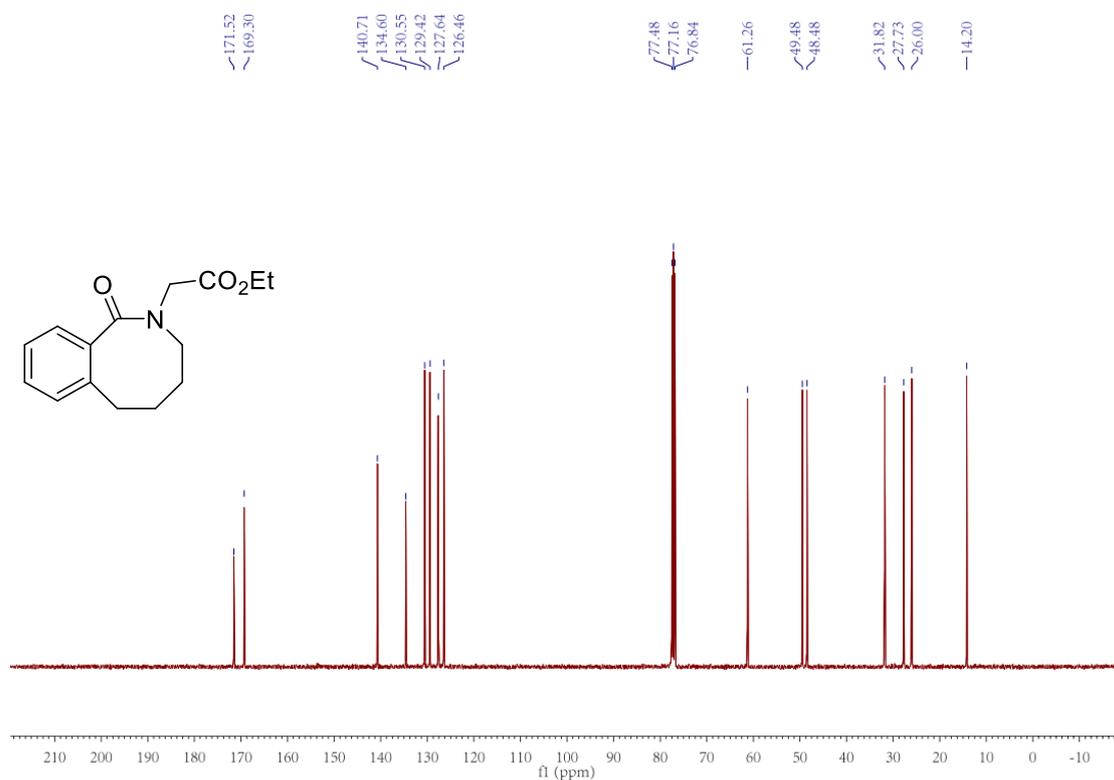


N-(2-Ethoxy-2-oxoethyl)tetrahydrobenzoazocin-1(2H)-one (**10fa**)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

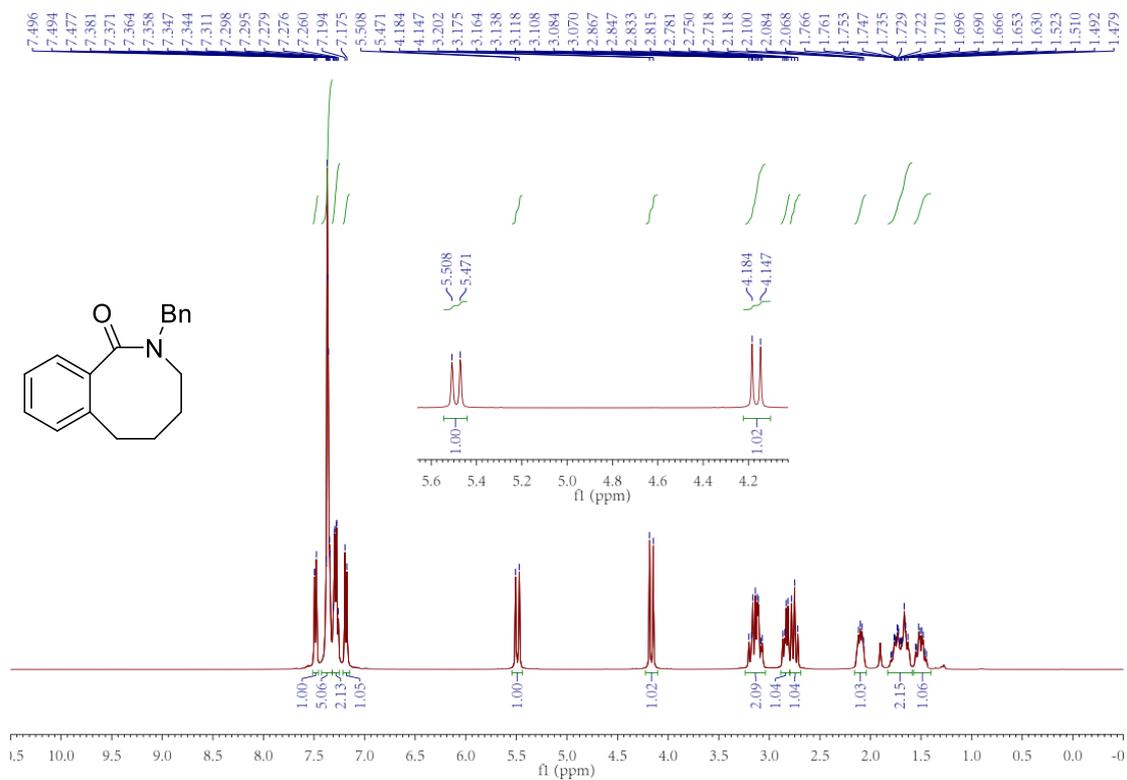


<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

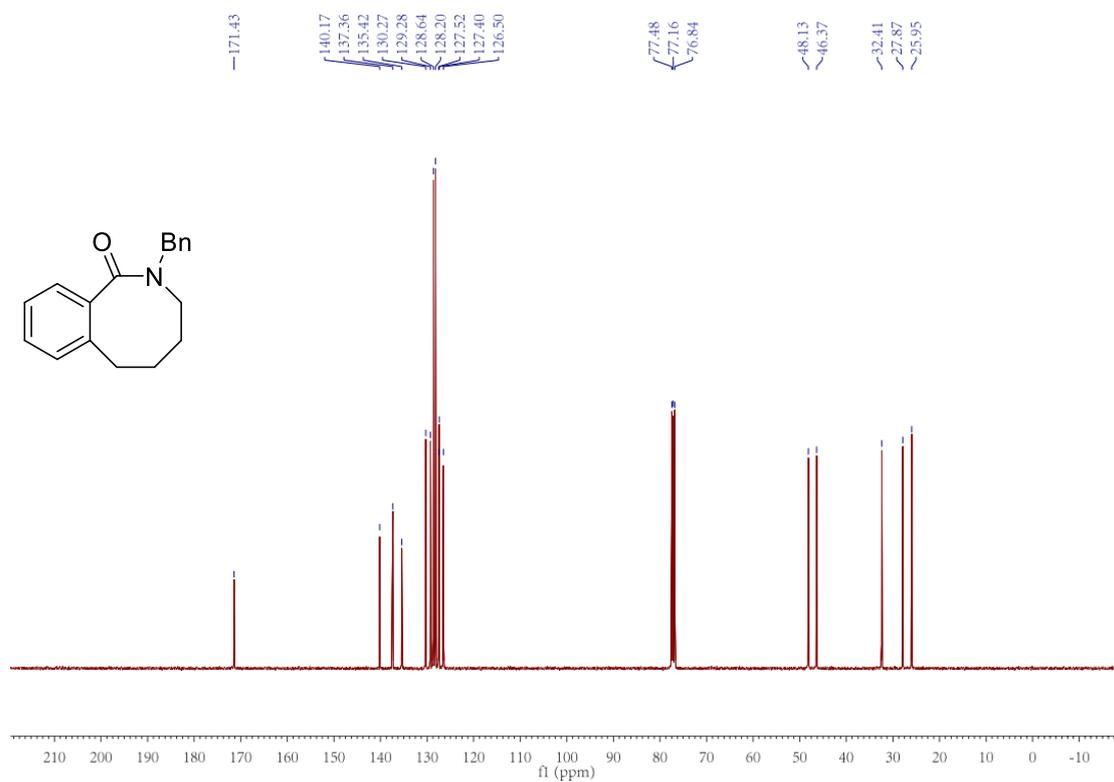


# N-Benzyltetrahydrobenzoazocin-1(2H)-one (**10ga**)

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )

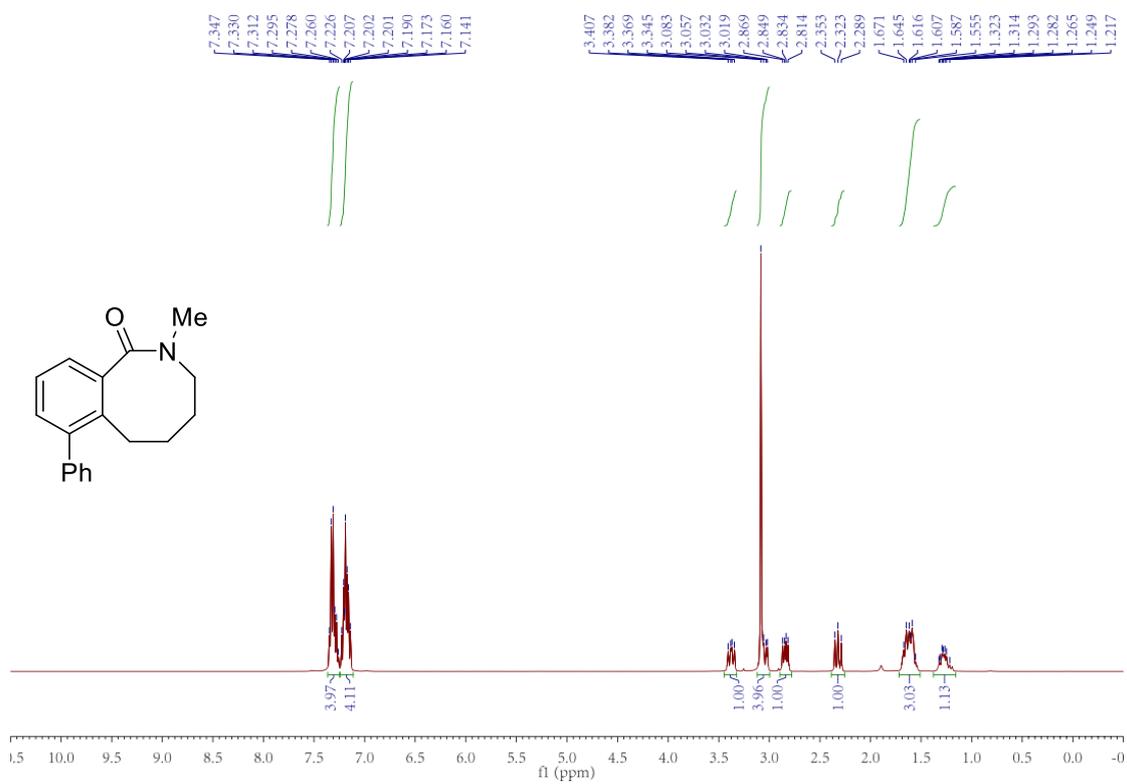


$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

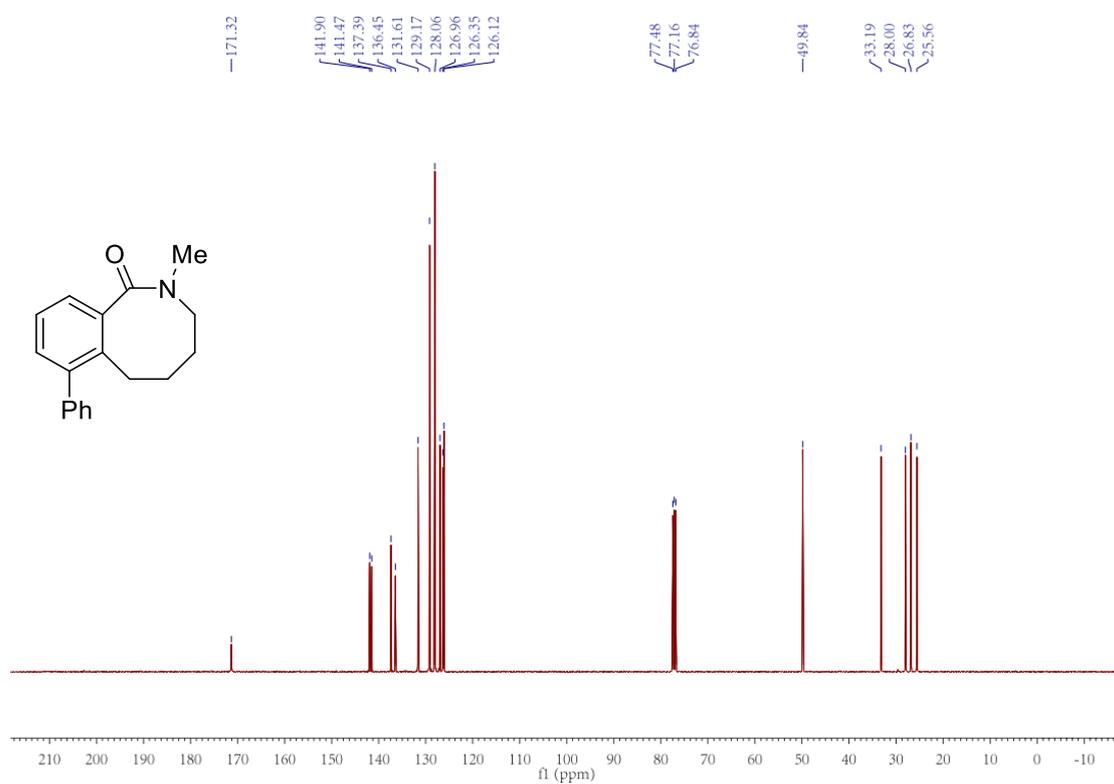


N-Methyl-7-phenyltetrahydrobenzoazocin-1(2H)-one (**10ka**)

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )

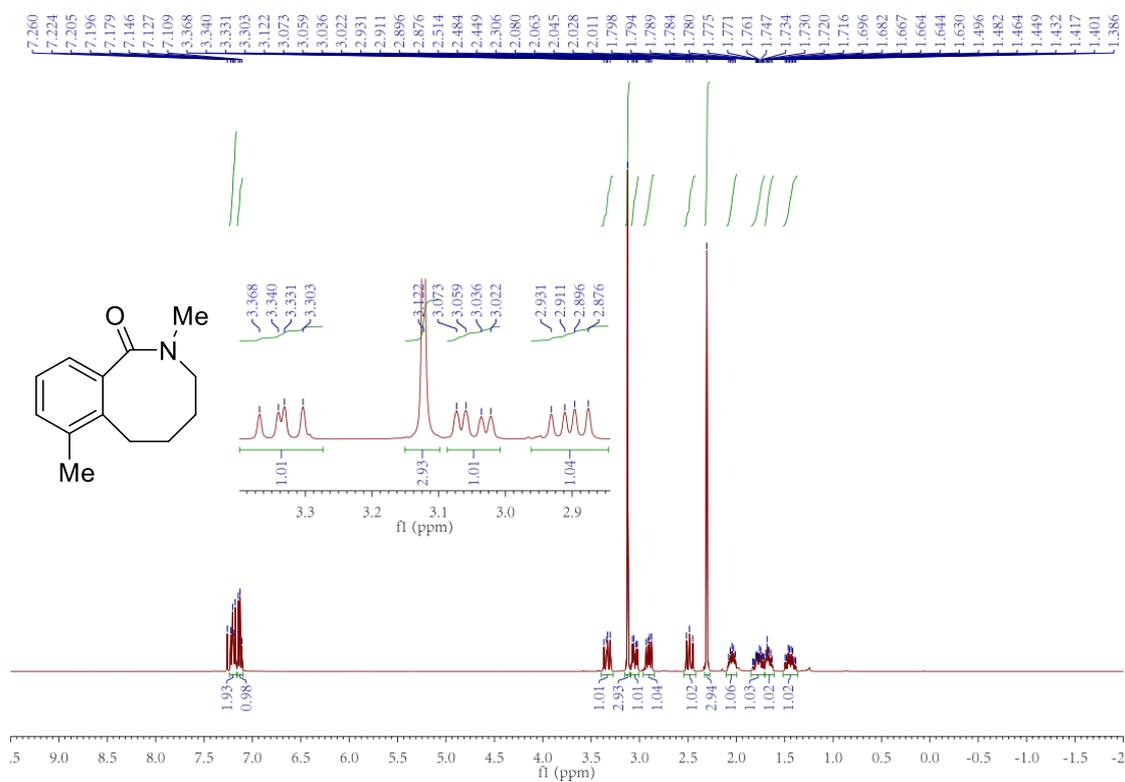


$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

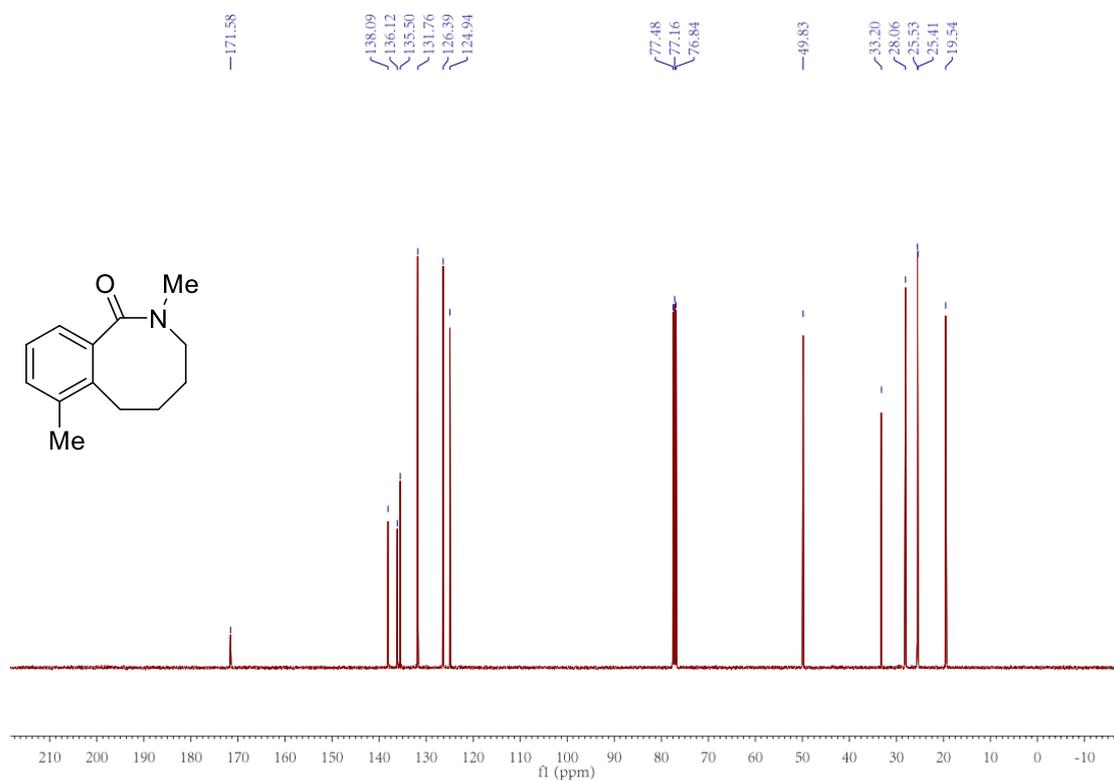


N,7-Dimethyltetrahydrobenzoazocin-1(2H)-one (**10la**)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

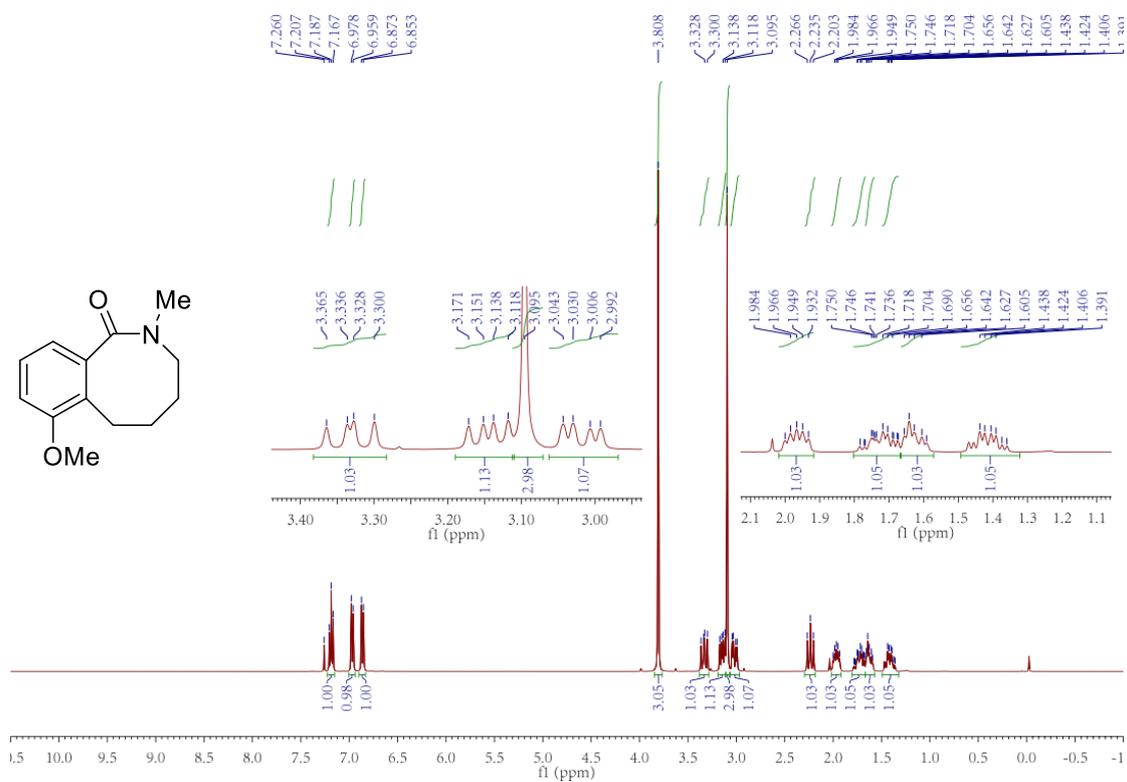


<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

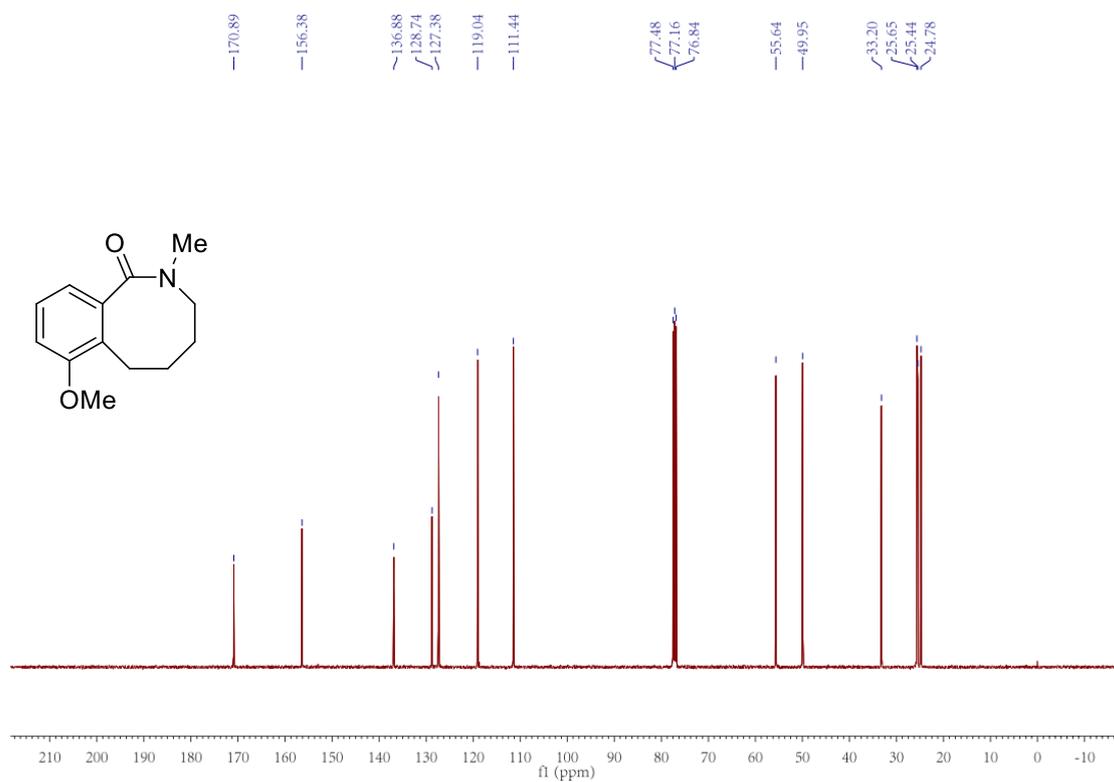


N-Methyl-7-methoxytetrahydrobenzoazocin-1(2H)-one (**10ma**)

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )

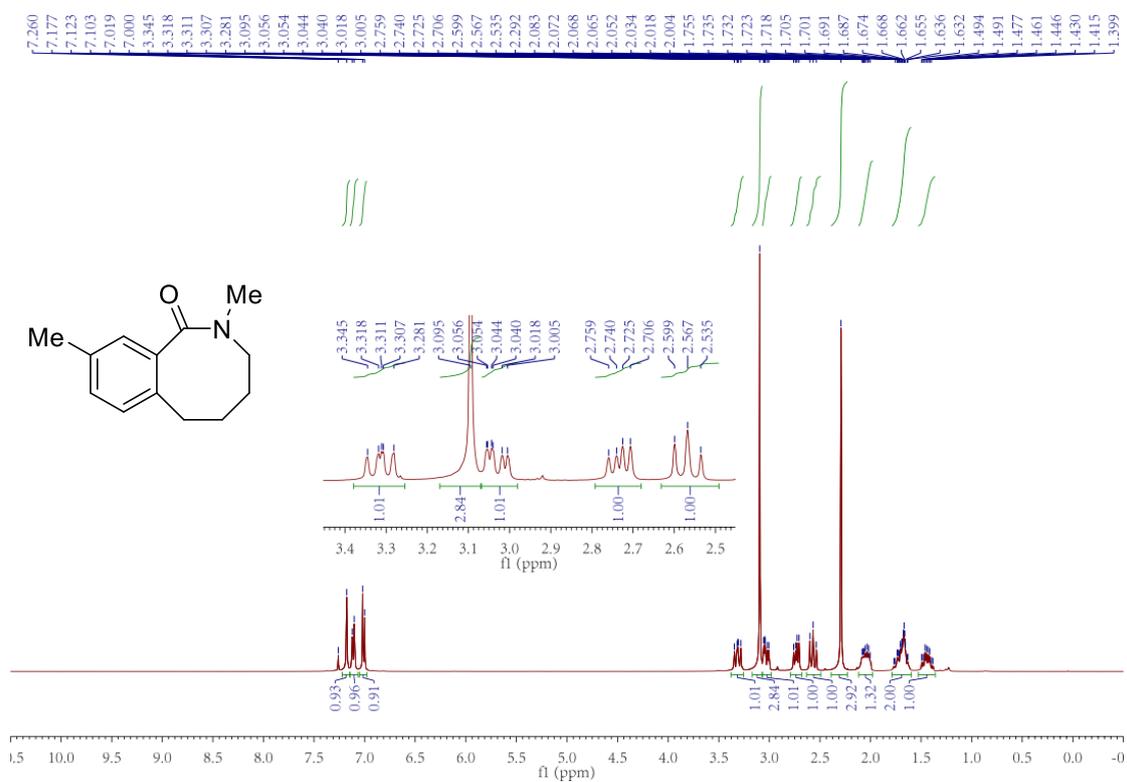


$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

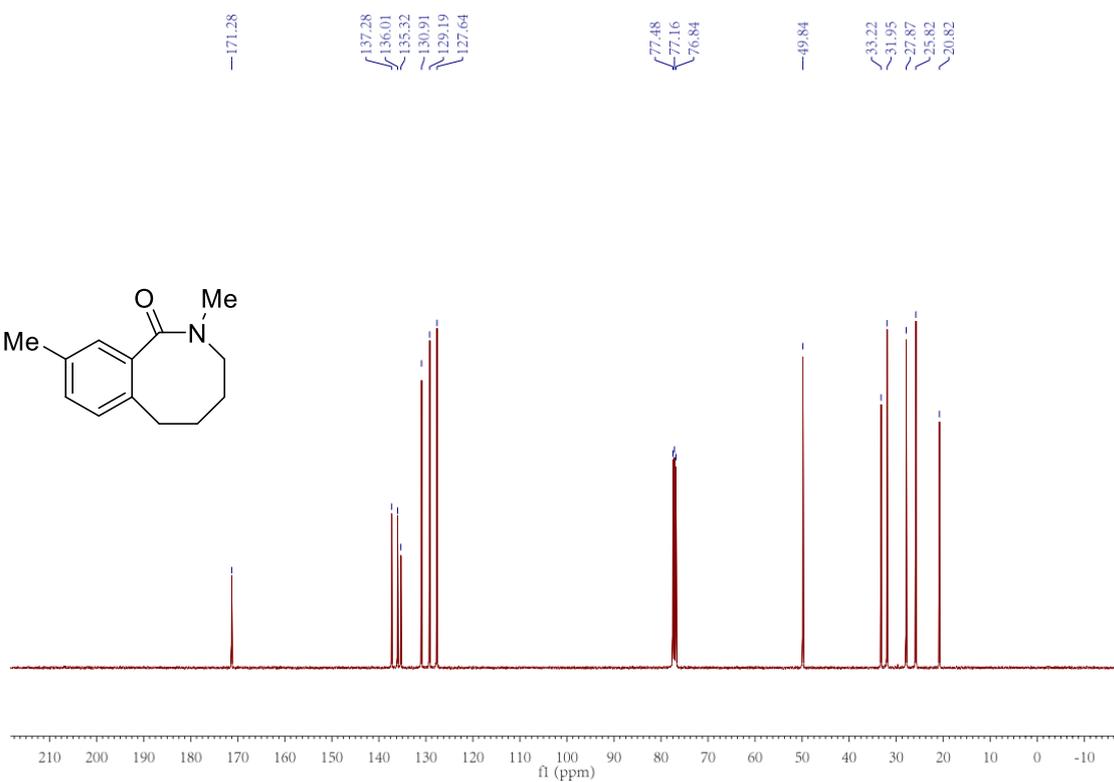


N,9-Dimethyltetrahydrobenzoazocin-1(2H)-one (**10na**)

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )

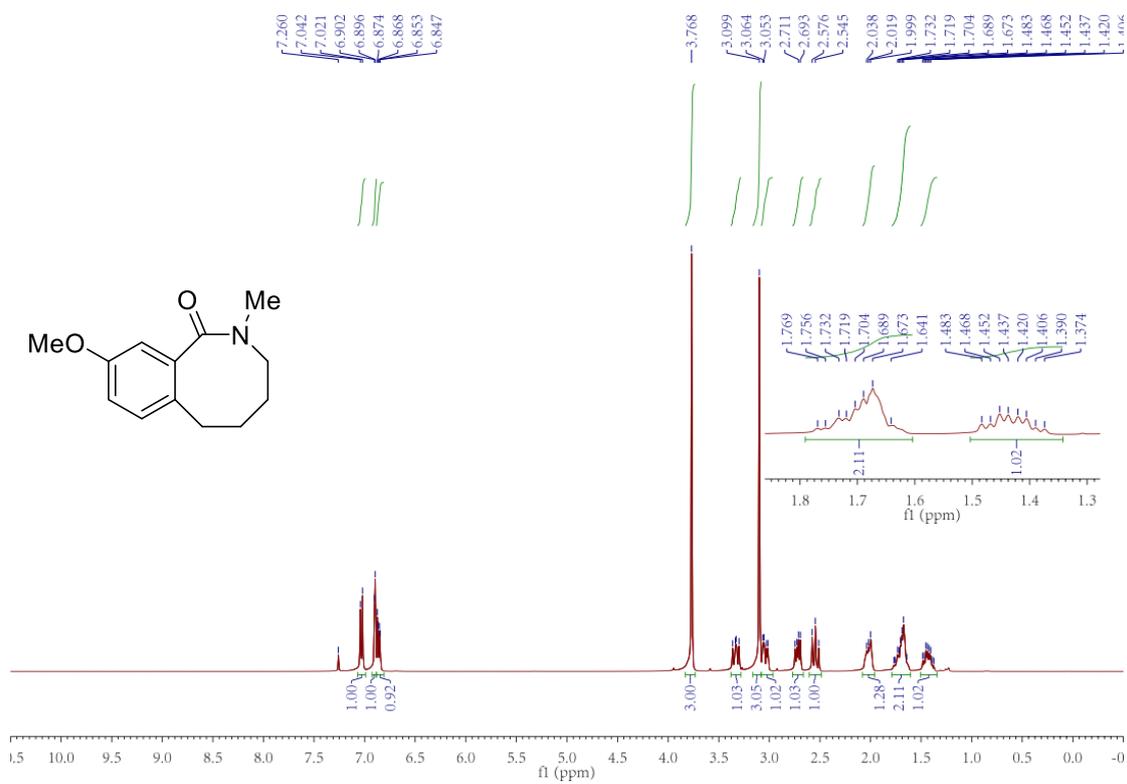


$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

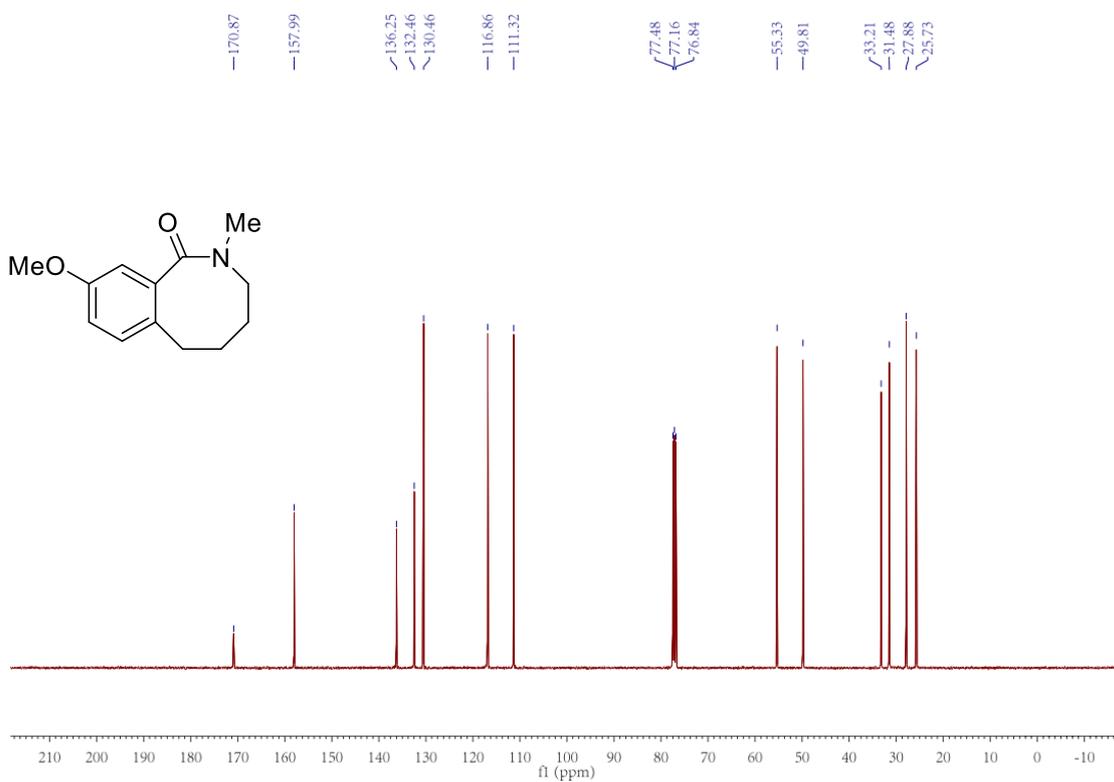


N-Methyl-9-methoxytetrahydrobenzoazocin-1(2H)-one (**100a**)

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )

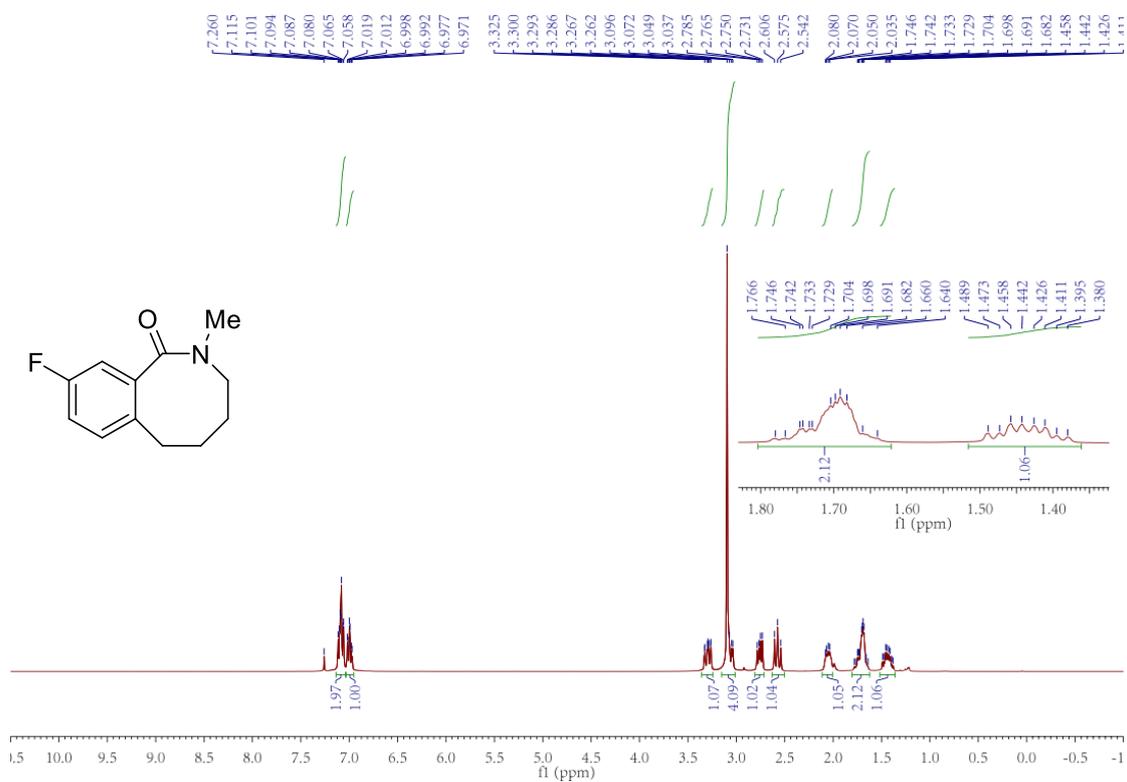


$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

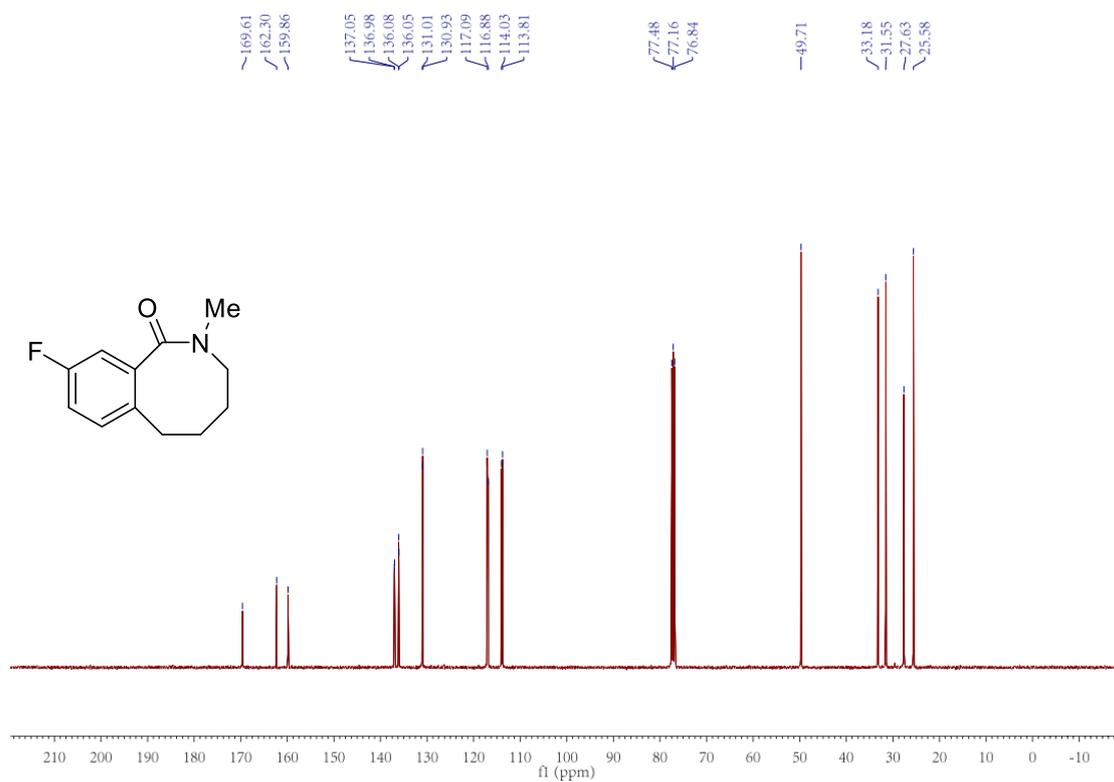


# N-Methyl-9-fluorotetrahydrobenzoazocin-1(2H)-one (10pa)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

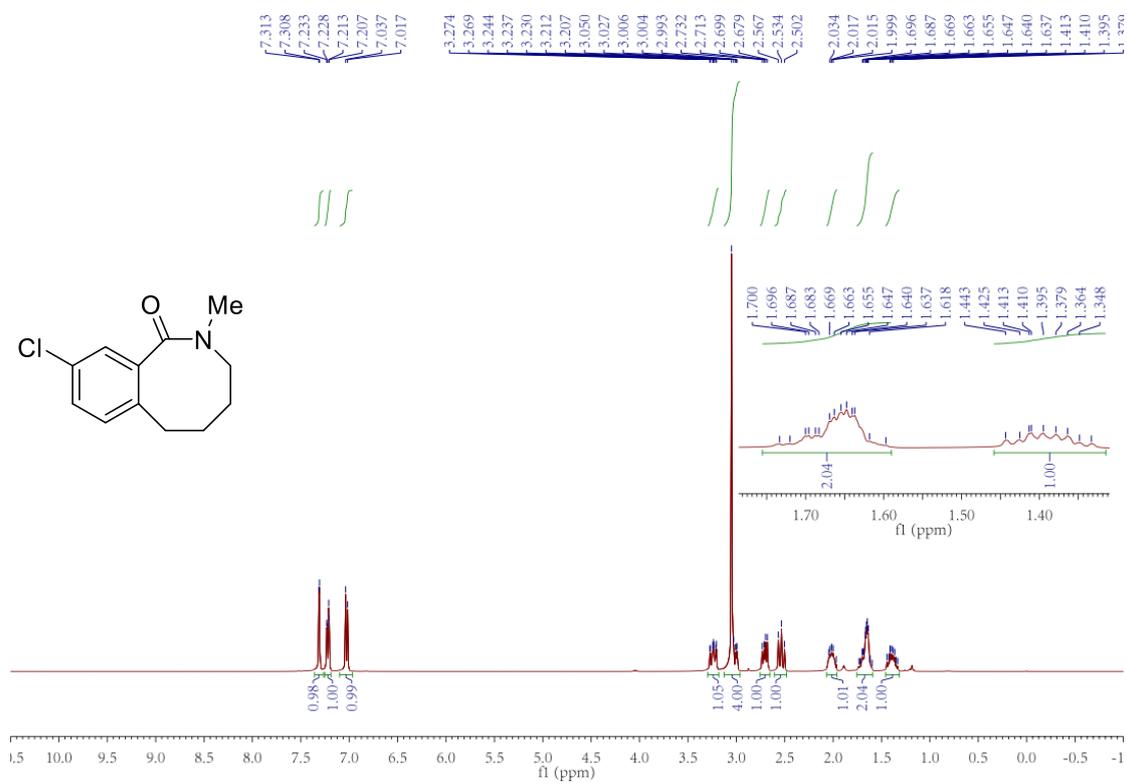


<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

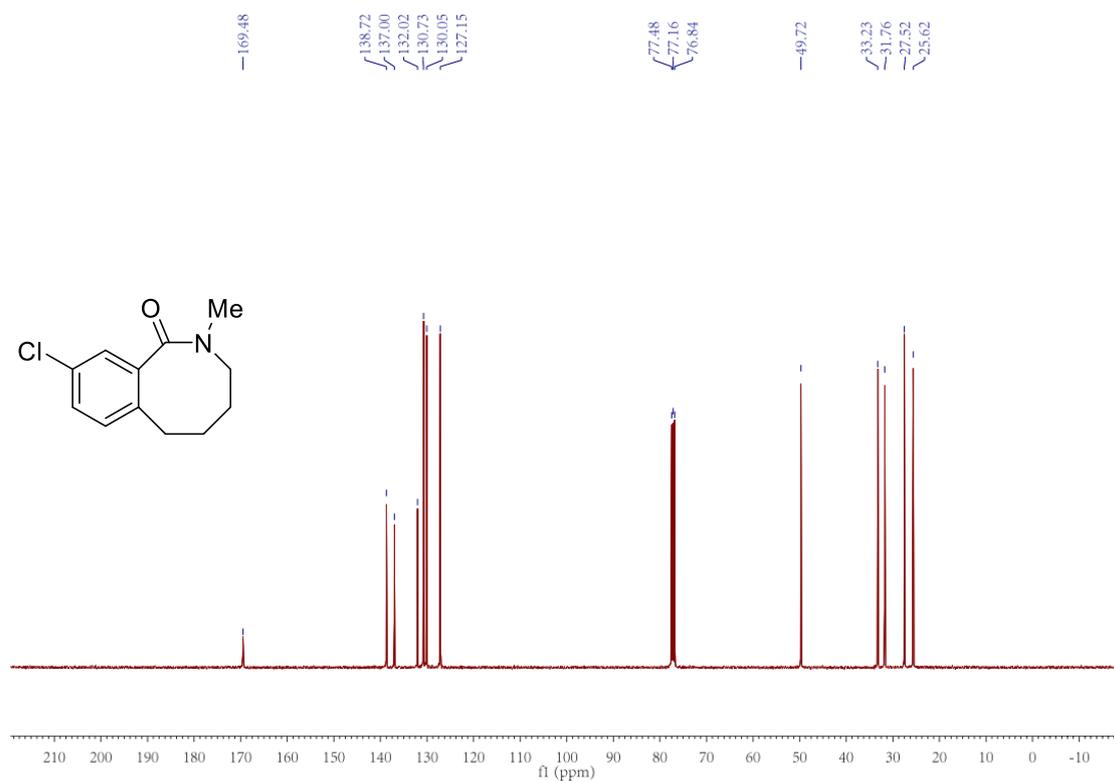


N-Methyl-9-chlorotetrahydrobenzoazocin-1(2H)-one (**10qa**)

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )

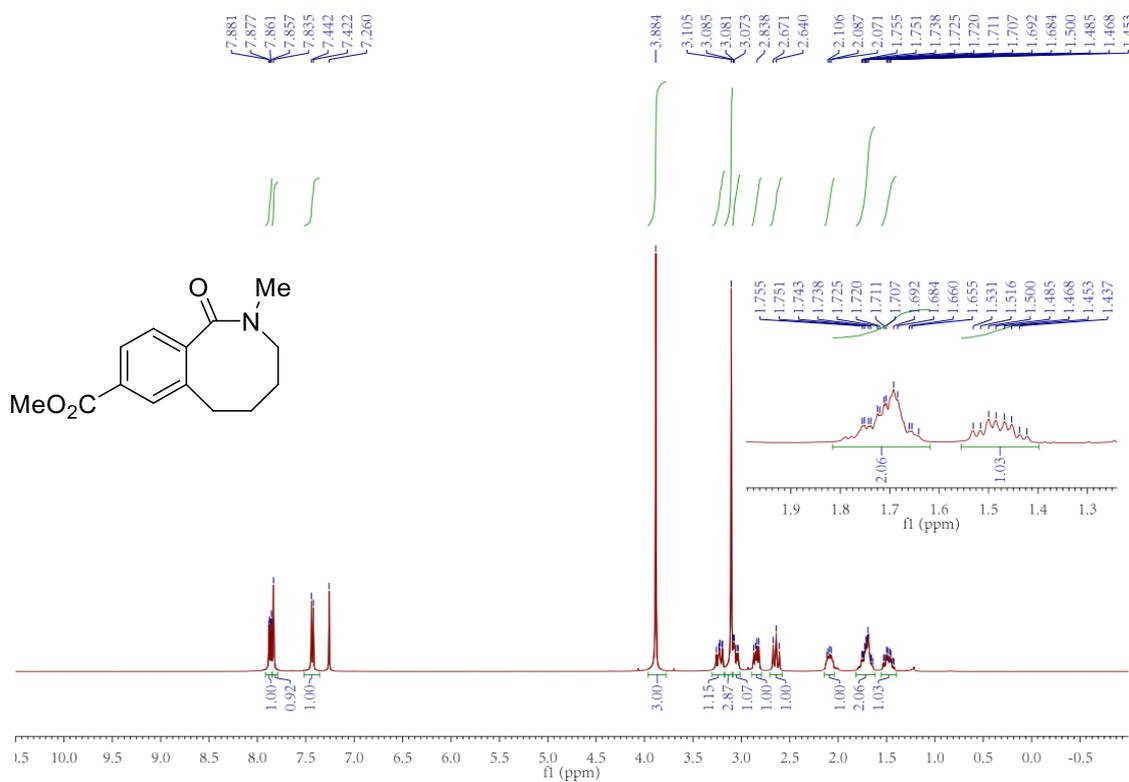


$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

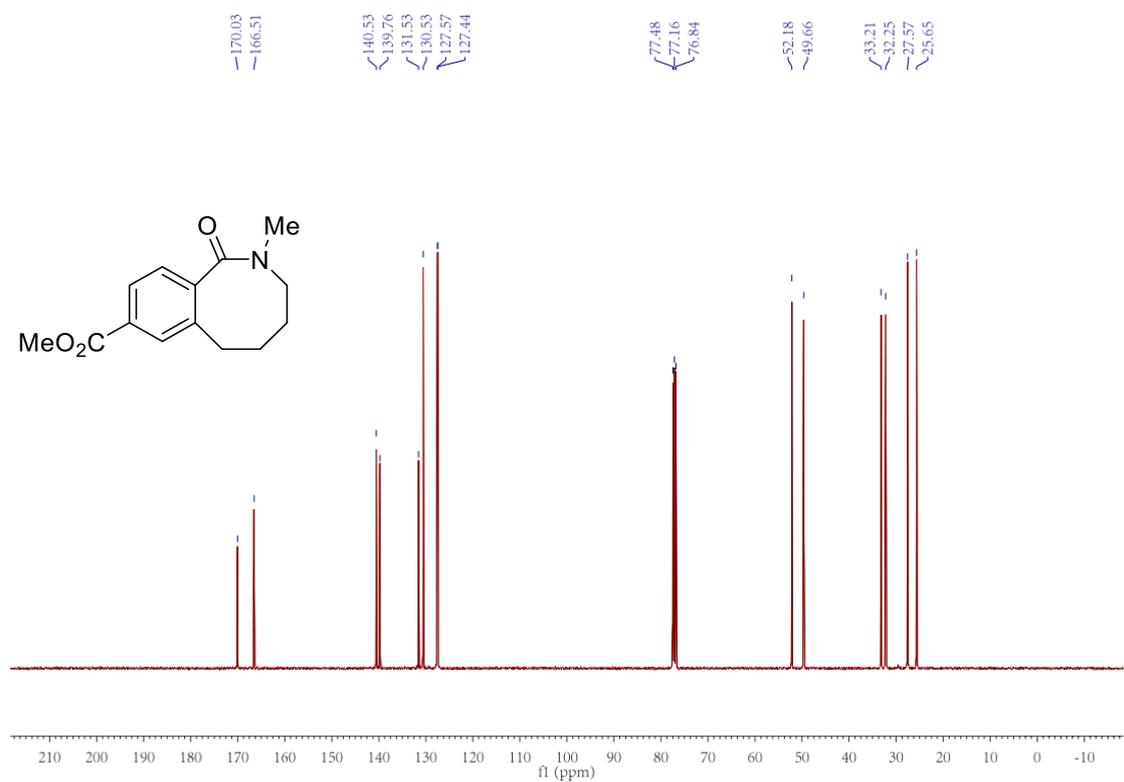


N-Methyl-8-(methoxycarbonyl)tetrahydrobenzazocin-1(2H)-one (**10sa**)

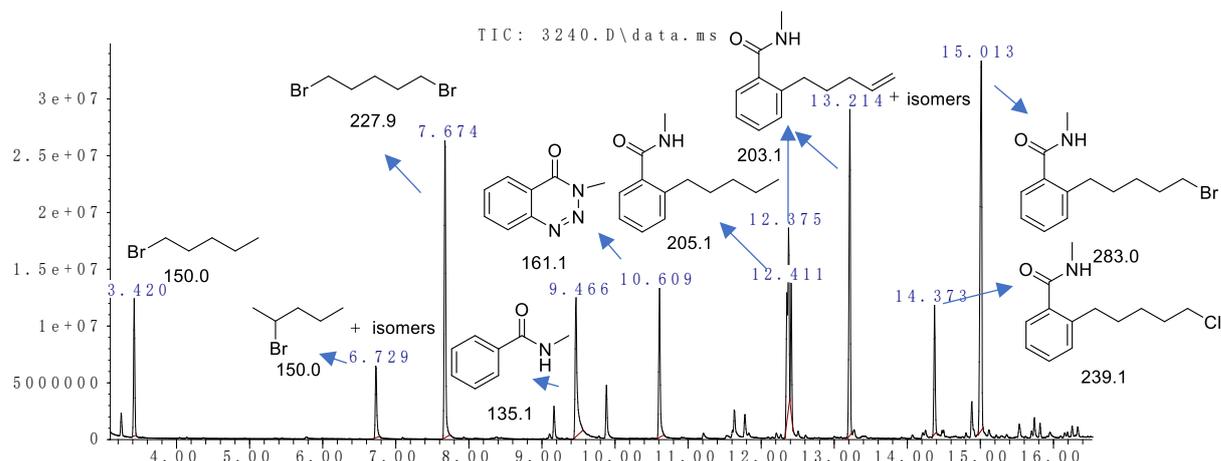
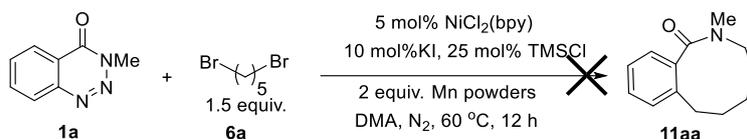
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )



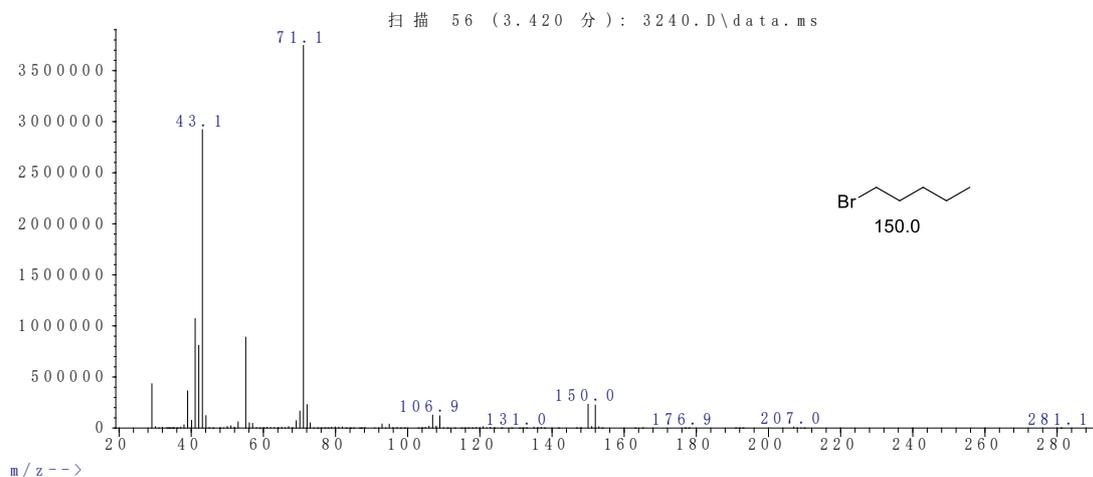
### GC-MS of reaction mixture from 1a with 6a



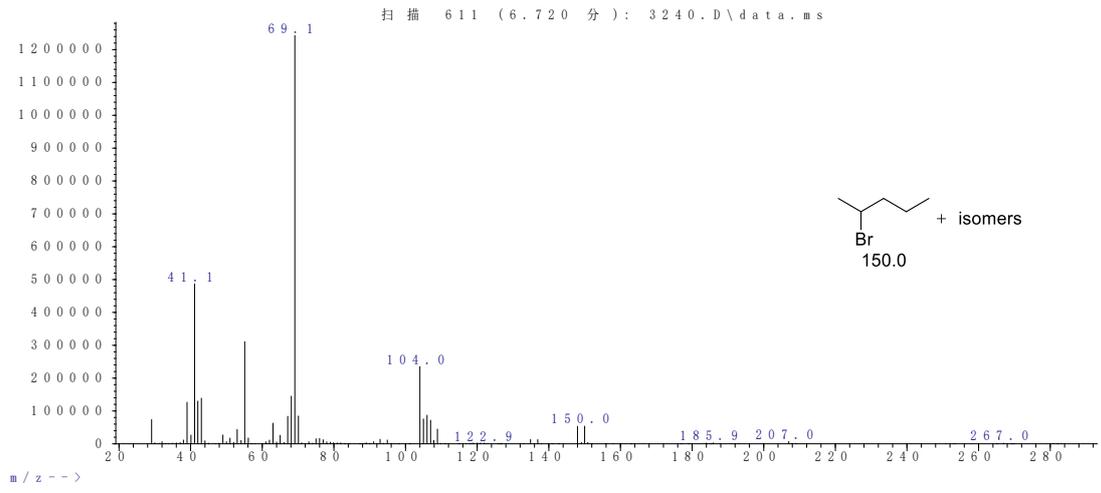
peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max	%of total
1	3.420	52	56	61	M	12087531	138673217	24.75%	5.446%
2	6.729	609	612	622	M	6571673	89484833	15.97%	3.514%
3	7.674	767	771	783	M	26923790	379566072	67.75%	14.906%
4	9.466	1068	1073	1089	M	12379451	239937390	42.83%	9.423%
5	10.609	1260	1265	1276	M	13144524	184944589	33.01%	7.263%
6	12.375	1554	1562	1565	M2	15884843	309902857	55.32%	12.171%
7	12.411	1565	1568	1572	M	11458886	121009201	21.60%	4.752%
8	13.214	1697	1703	1708	M	28697585	386915665	69.06%	15.195%
9	14.373	1894	1898	1903	M	11329033	135647005	24.21%	5.327%
10	15.013	1999	2006	2010	M	35218389	560243105	100.00%	22.002%

Sum of corrected areas: 2546323933

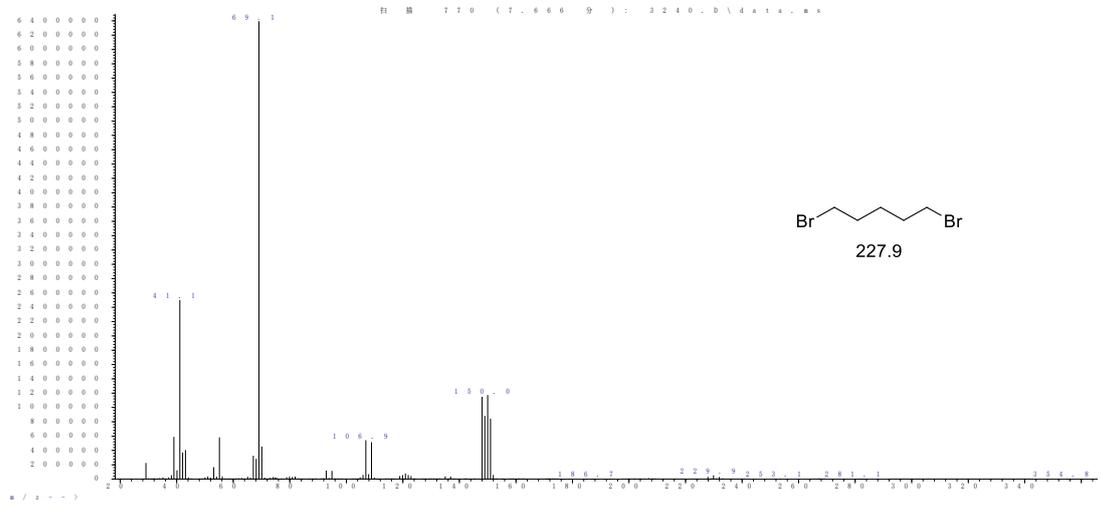
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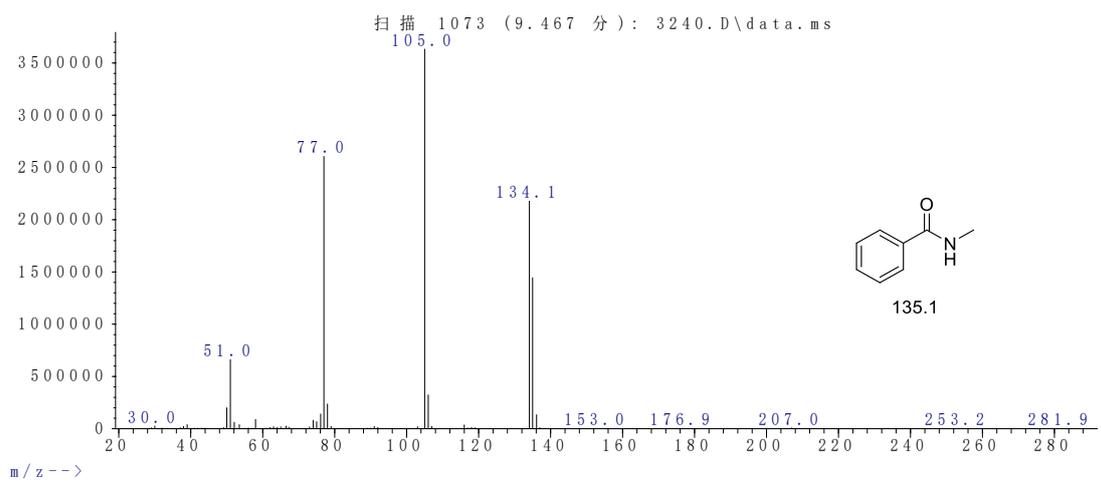
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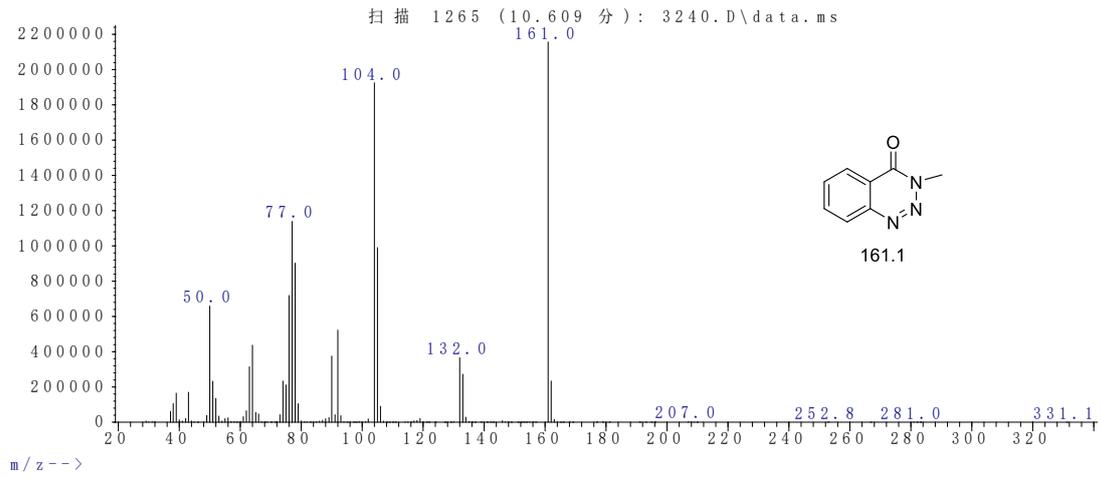
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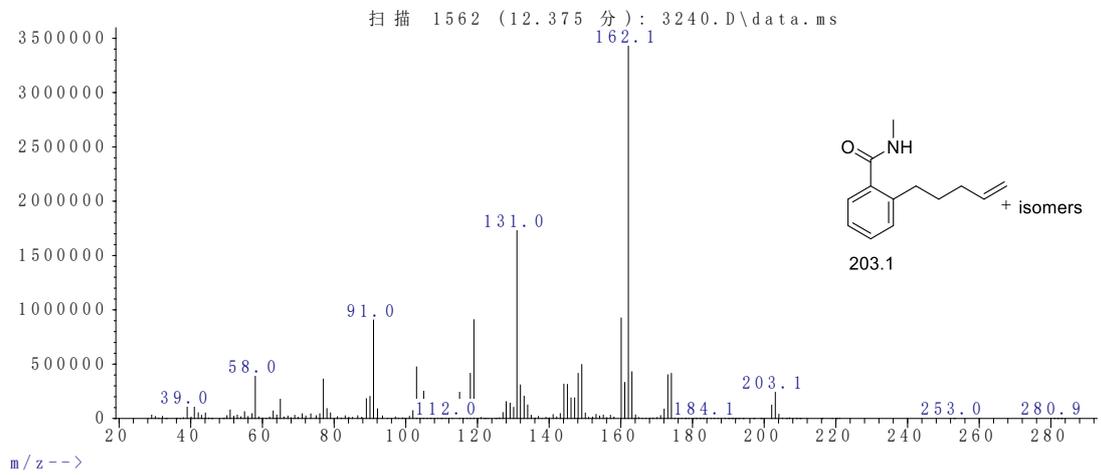
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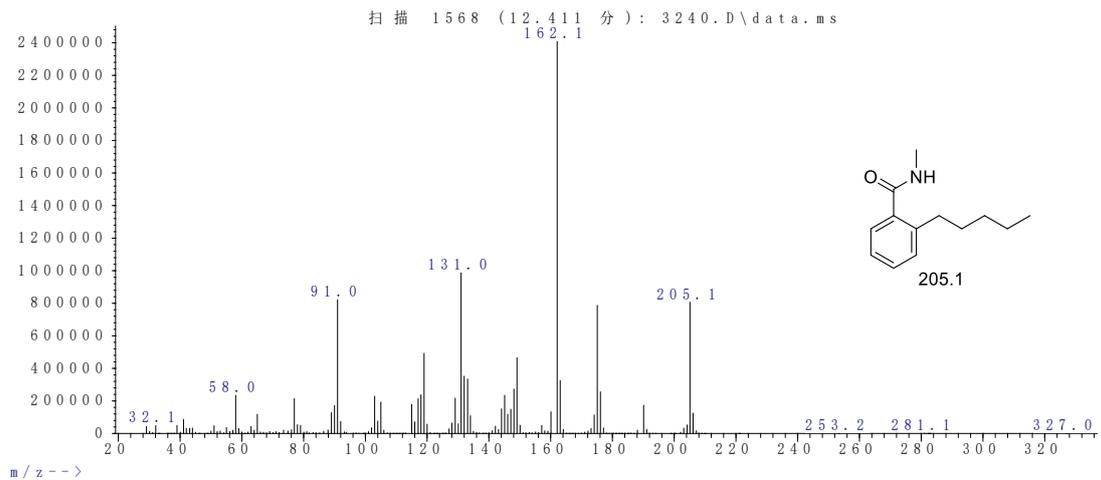
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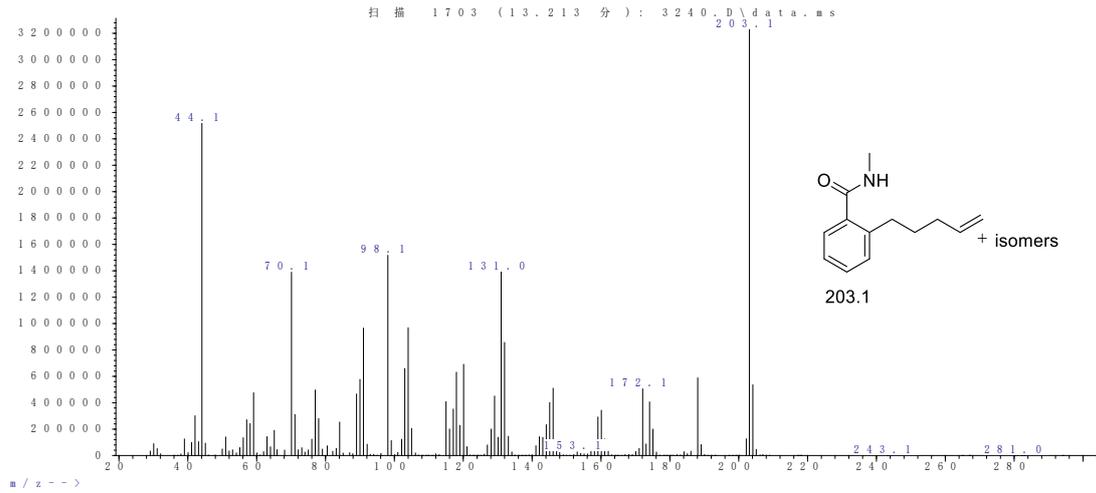
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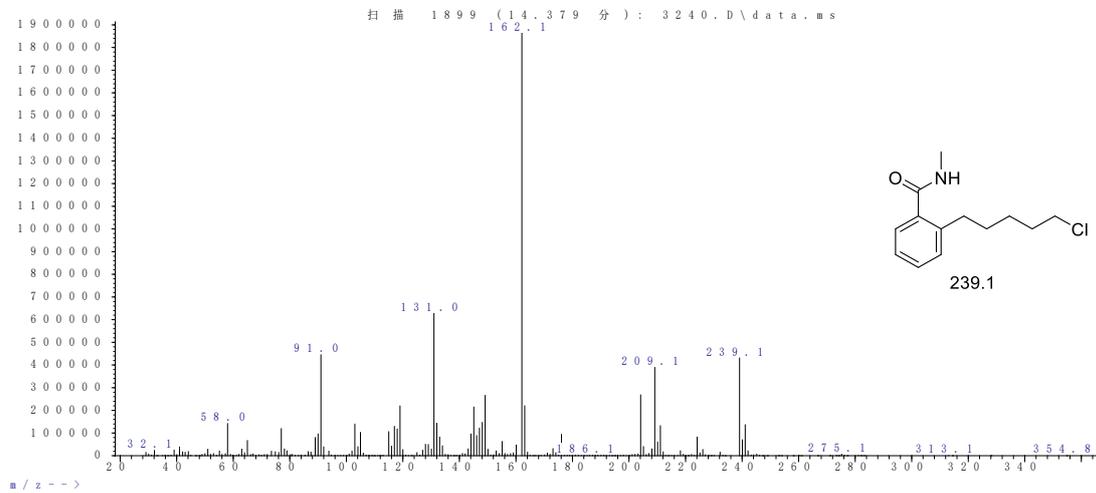
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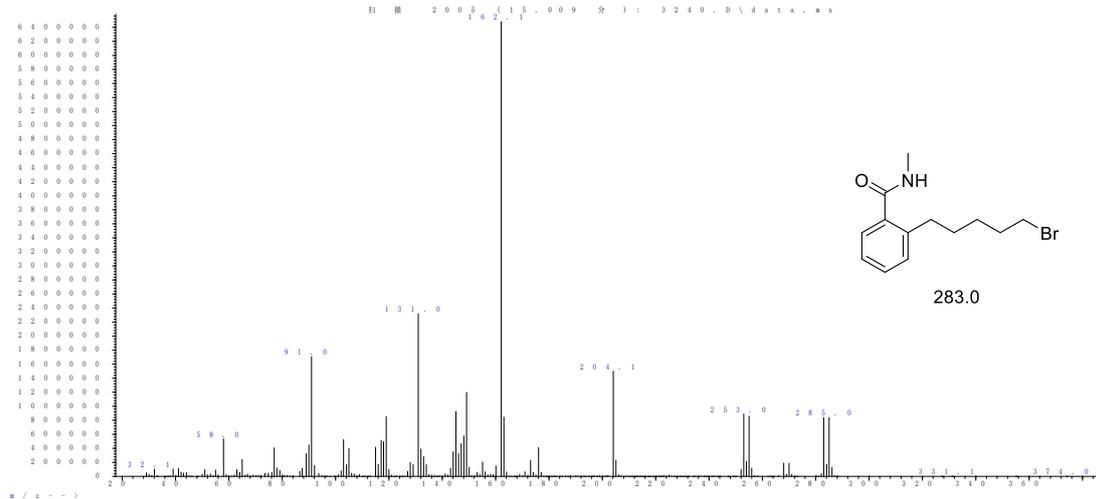
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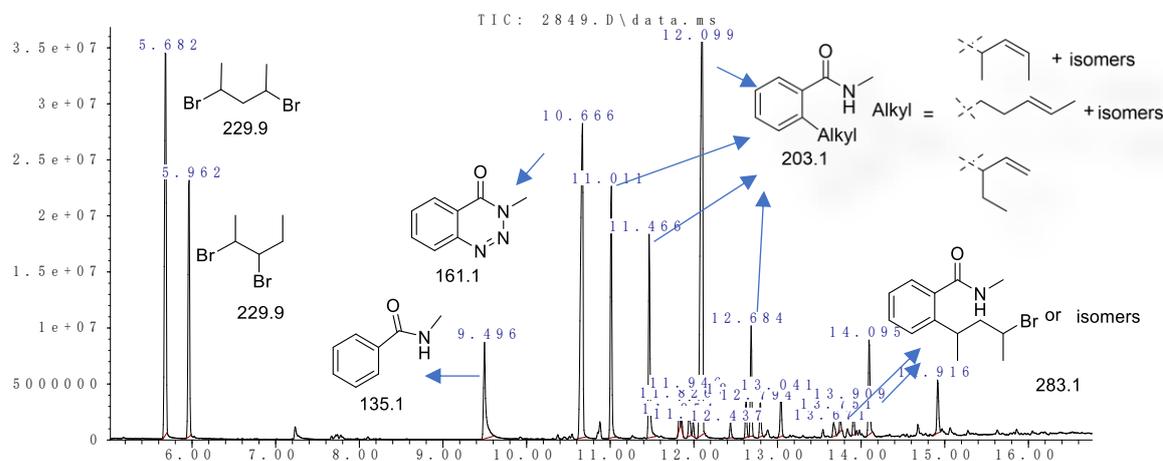
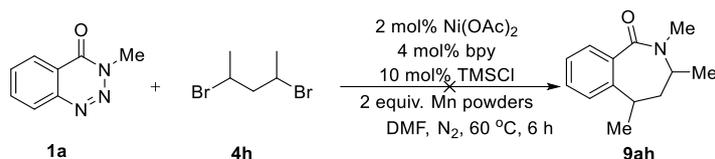
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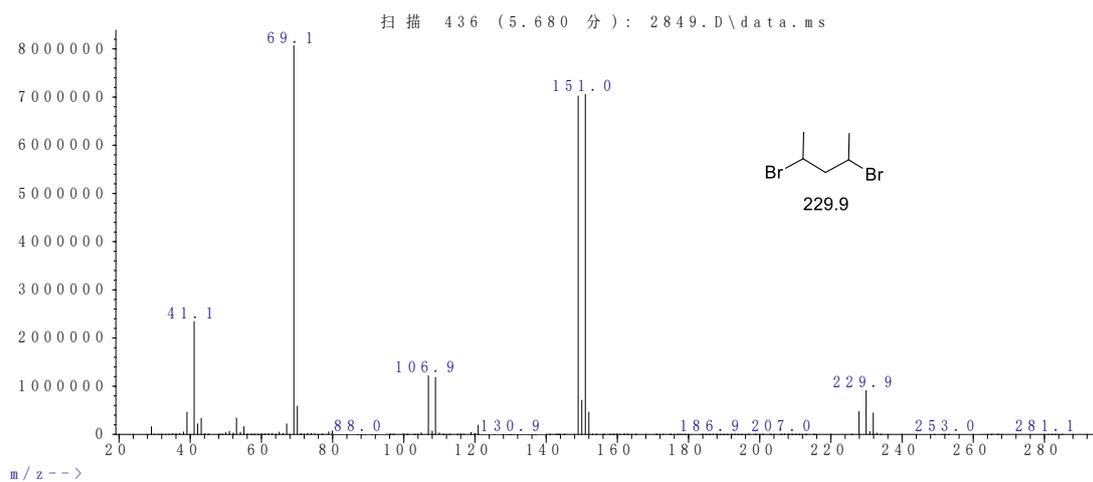
### GC-MS of reaction mixture from 1a with 4h



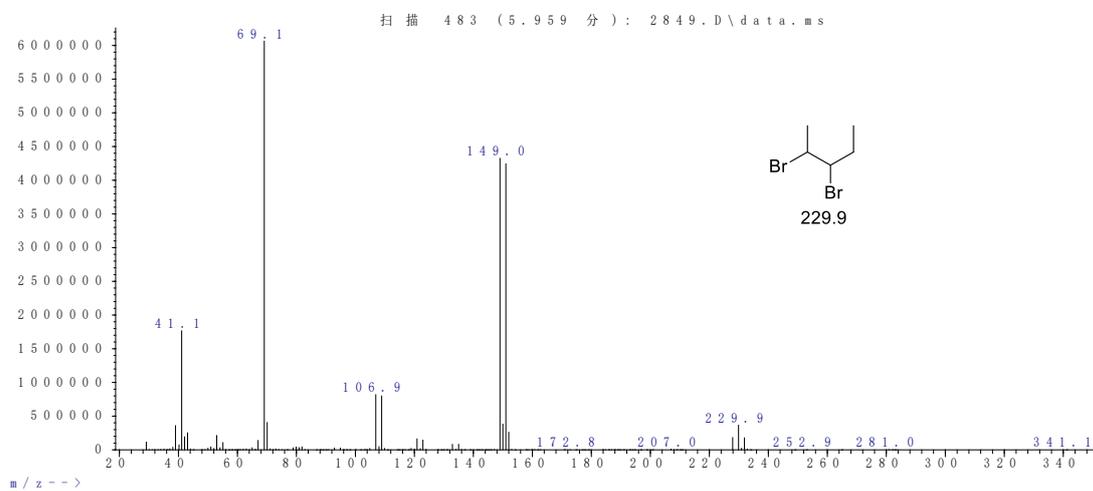
peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max	%of total
1	5.682	431	436	440	M	35006554	504479858	64.35%	14.572%
2	5.962	479	484	488	M	23867976	302095346	38.54%	8.726%
3	9.496	1072	1078	1097	M	8606468	160856290	20.52%	4.646%
4	10.666	1265	1275	1283	M	28461600	572562909	73.04%	16.539%
5	11.011	1328	1333	1344	M	23234295	285352135	36.40%	8.243%
6	11.466	1405	1409	1422	M	18229004	231501562	29.53%	6.687%
7	11.826	1465	1470	1472	M	2606472	26498593	3.38%	0.765%
8	11.854	1472	1474	1478	M	1101176	10039038	1.28%	0.290%
9	11.946	1486	1490	1494	M	4015714	46515857	5.93%	1.344%
10	11.992	1495	1498	1502	M	1327980	14506358	1.85%	0.419%
11	12.099	1506	1516	1521	M2	39268424	783927595	100.00%	22.644%
12	12.437	1569	1572	1578	M	1366912	16519438	2.11%	0.477%
13	12.624	1600	1604	1608	M	3637129	41630833	5.31%	1.203%
14	12.684	1609	1614	1619	M	9863662	116875778	14.91%	3.376%
15	12.794	1629	1633	1638	M	3138557	38975043	4.97%	1.126%
16	13.041	1668	1674	1679	M	3941543	51827573	6.61%	1.497%
17	13.671	1776	1780	1786	M	1237203	20627901	2.63%	0.596%
18	13.751	1790	1793	1797	M	1829576	18666118	2.38%	0.539%
19	13.909	1816	1820	1823	M	2996455	32517055	4.15%	0.939%
20	14.095	1847	1851	1858	M2	8645076	117867834	15.04%	3.405%
21	14.916	1981	1989	1995	M	4831231	68116581	8.69%	1.968%

Sum of corrected areas: 3461959696

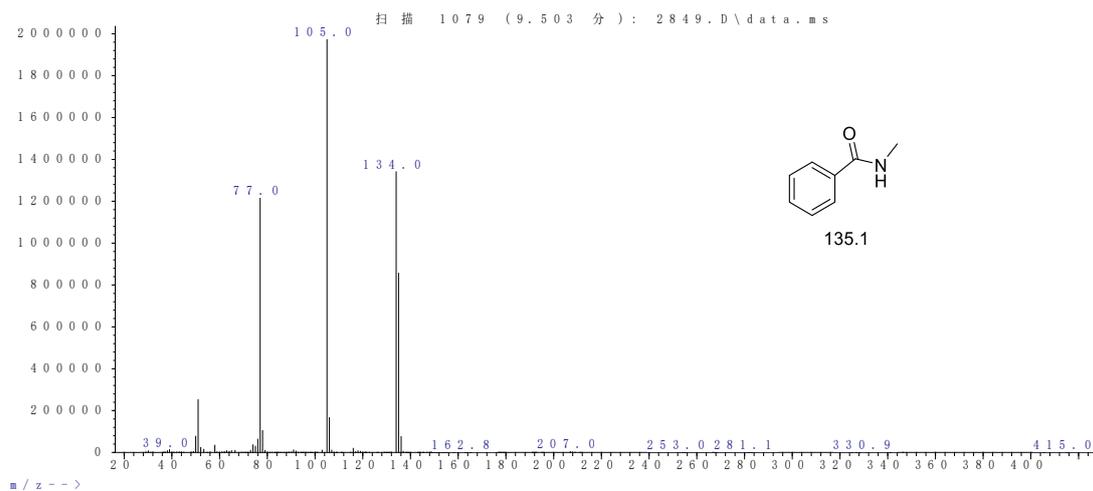
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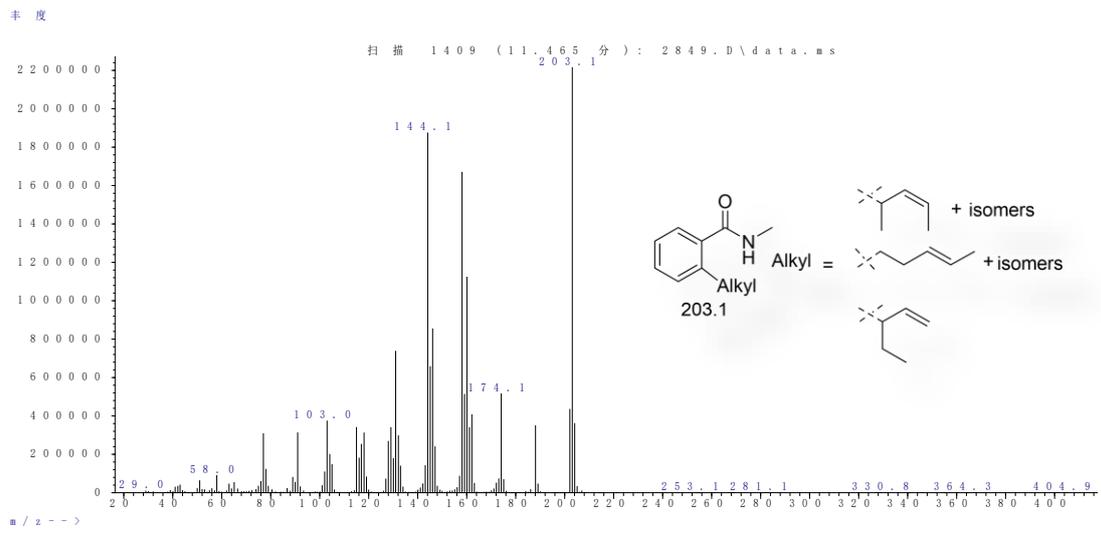
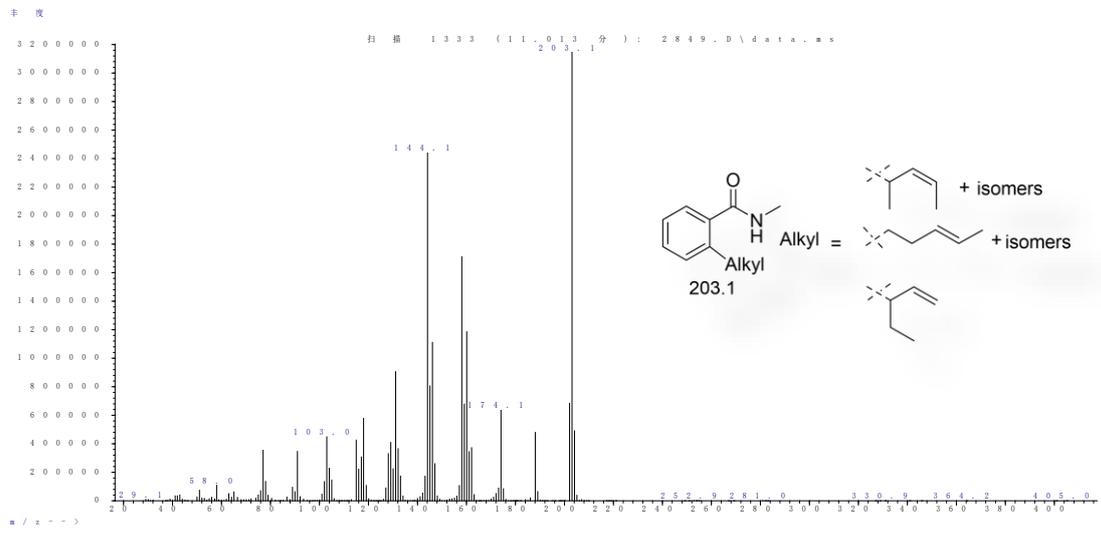
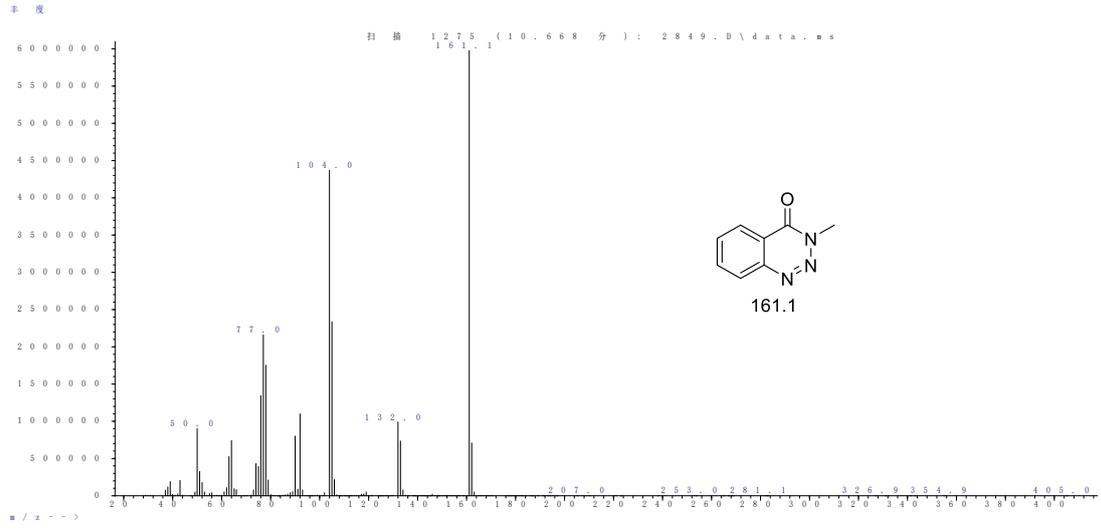


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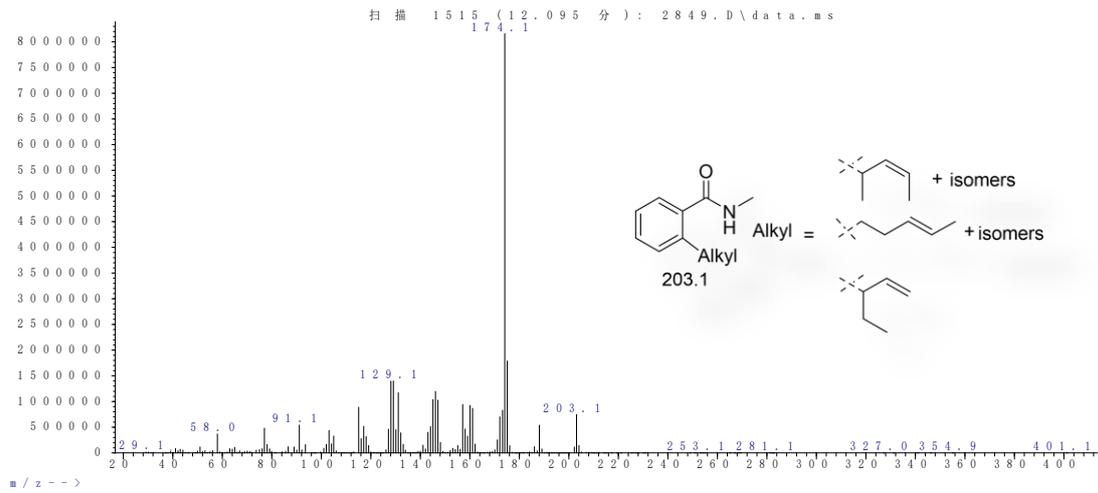


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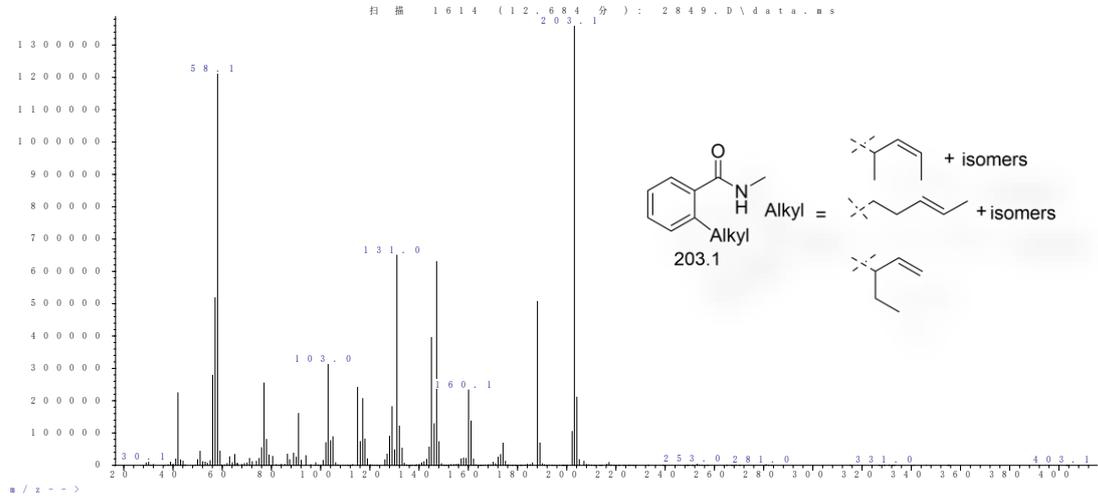




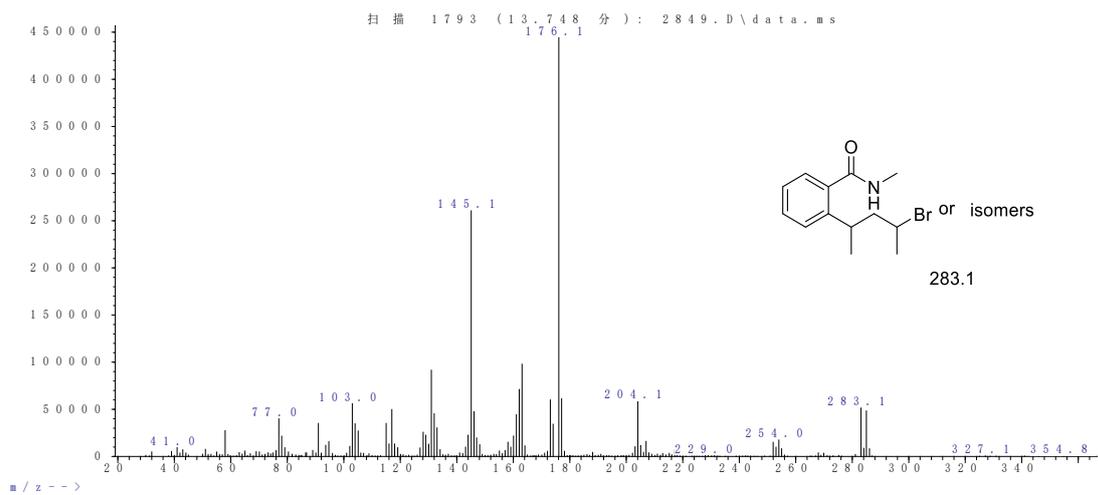
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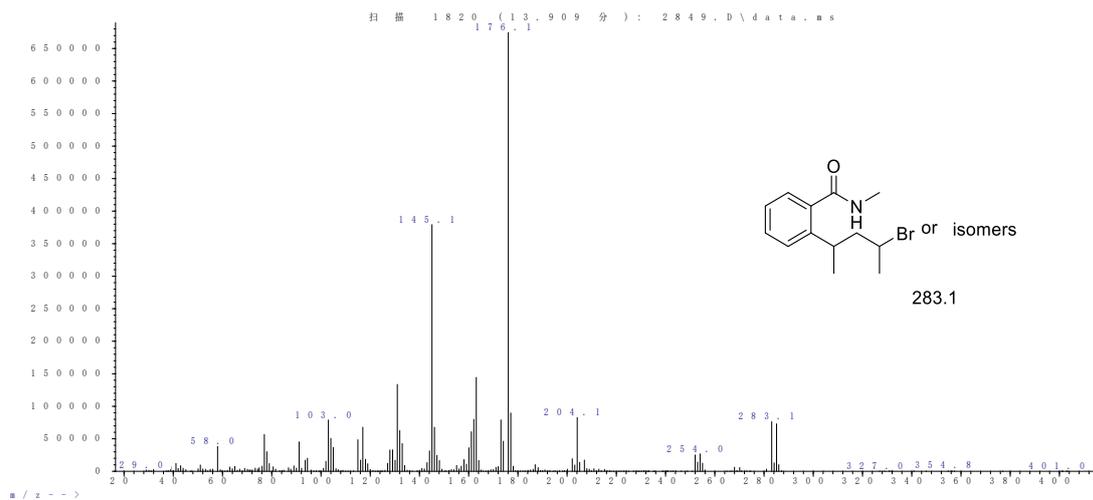
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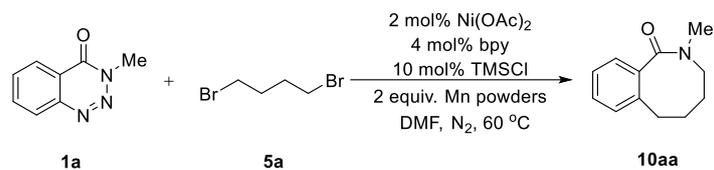
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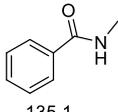
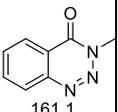
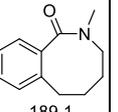
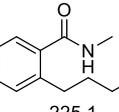
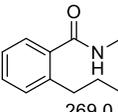
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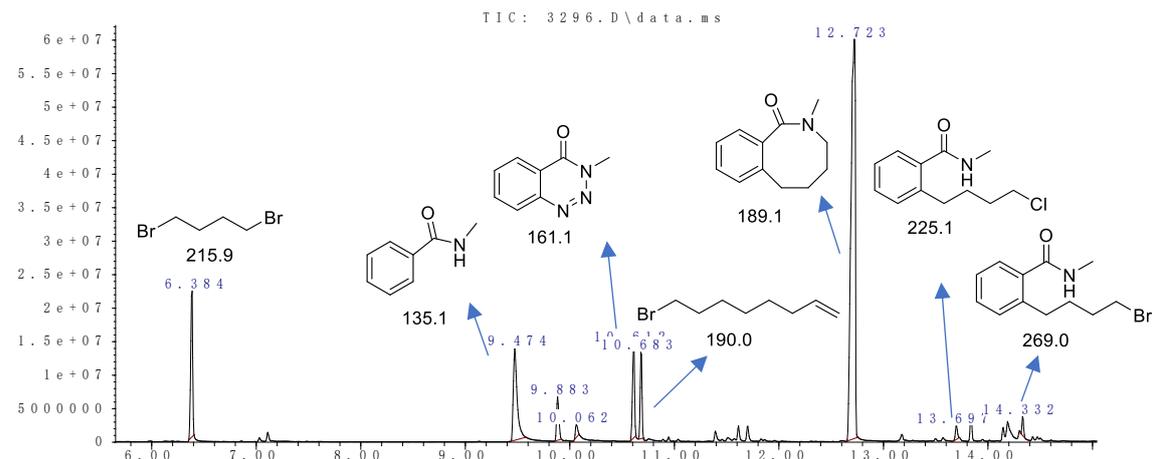
**GC-MS of reaction mixture from 1a with 5a**



**Table S1.** Composition of the reaction mixture at 8 h and at 16 h after adding one more dose of catalyst after 8 h

Condition \ Component /ratio%	 135.1	 161.1	 189.1	 225.1	 269.0
8 h	11.916	6.620	59.853	0.967	1.075
8 h+8 h (2 <sup>nd</sup> dose catalyst)	10.946	0	72.447	0.883	3.076

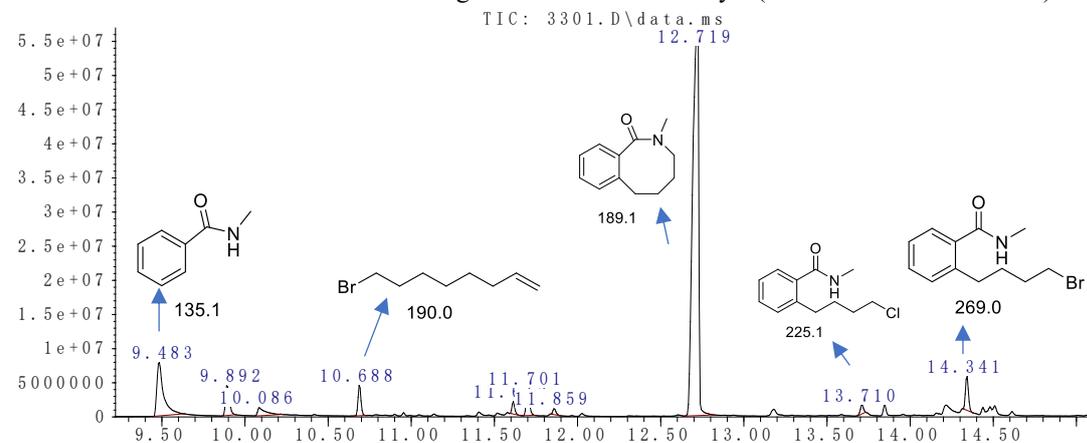
a. GC-MS of reaction mixture after 8 h at 2 mol% catalyst loading



peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	Corr. % max	%of total
1	6.384	550	555	559	M	22752246	288680101	16.54%	9.899%
2	9.474	1068	1074	1092	M	13689718	347490262	19.91%	11.916%
3	9.883	1139	1143	1149	M2	6491363	100368416	5.75%	3.442%
4	10.062	1169	1173	1177	M	1899600	28044452	1.61%	0.962%
5	10.612	1260	1266	1269	M	14726937	193039661	11.06%	6.620%
6	10.683	1273	1277	1281	M	13406072	153599693	8.80%	5.267%
7	12.723	1608	1621	1626	M2	62773985	1745423821	100.00%	59.853%
8	13.697	1780	1784	1789	M	2064896	28191662	1.62%	0.967%
9	14.332	1888	1891	1897	M	2858224	31351563	1.80%	1.075%

Sum of corrected areas: 2916189631

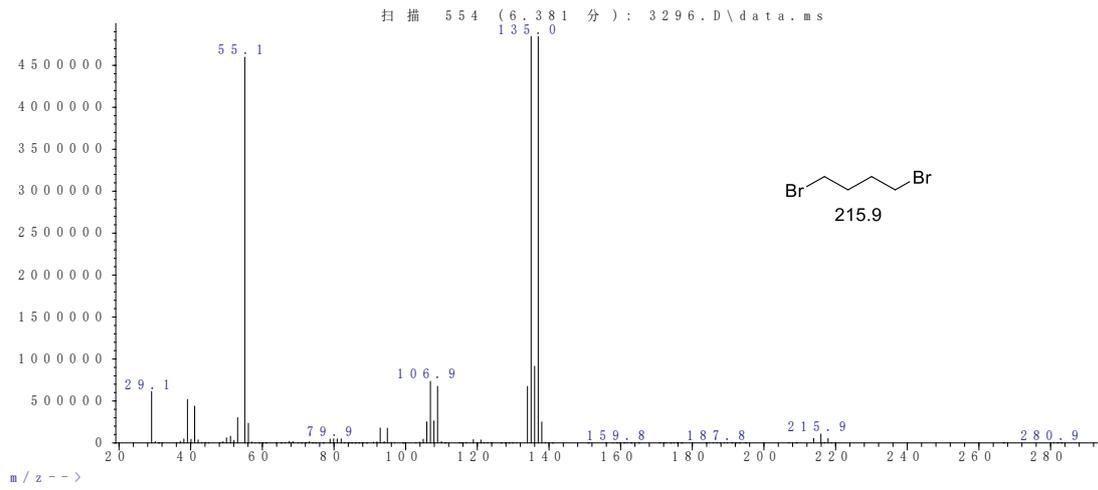
b. GC-MS of reaction mixture after adding one more dose of catalyst (2 mol% 8 h + 2 mol% 8 h)



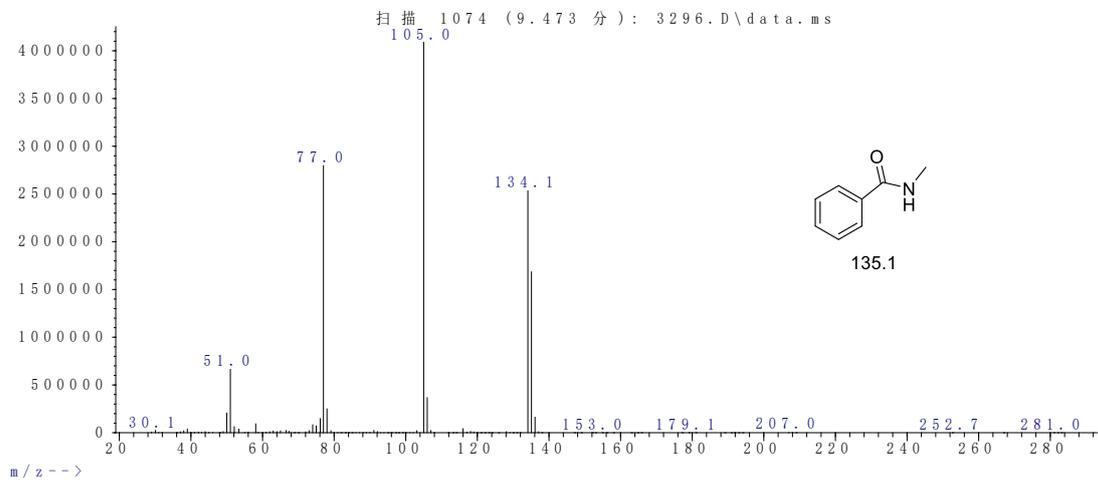
peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	Corr. % max	%of total
1	9.483	1070	1076	1101	M	7883074	219673921	15.11%	10.946%
2	9.892	1139	1144	1153	M2	4506778	72356139	4.98%	3.606%
3	10.086	1173	1177	1200	M2	1196497	39273440	2.70%	1.957%
4	10.688	1273	1278	1285	M	4580829	54937500	3.78%	2.738%
5	11.613	1431	1434	1440	M	1841064	20710708	1.42%	1.032%
6	11.701	1444	1449	1455	M	4190434	55610638	3.82%	2.771%
7	11.859	1472	1475	1481	M	870828	10917682	0.75%	0.544%
8	12.719	1608	1620	1636	M2	56774013	1453880396	100.00%	72.447%
9	13.710	1782	1787	1790	M	1335753	17725255	1.22%	0.883%
10	14.341	1889	1893	1899	M	5094553	61737013	4.25%	3.076%

Sum of corrected areas: 2006822692

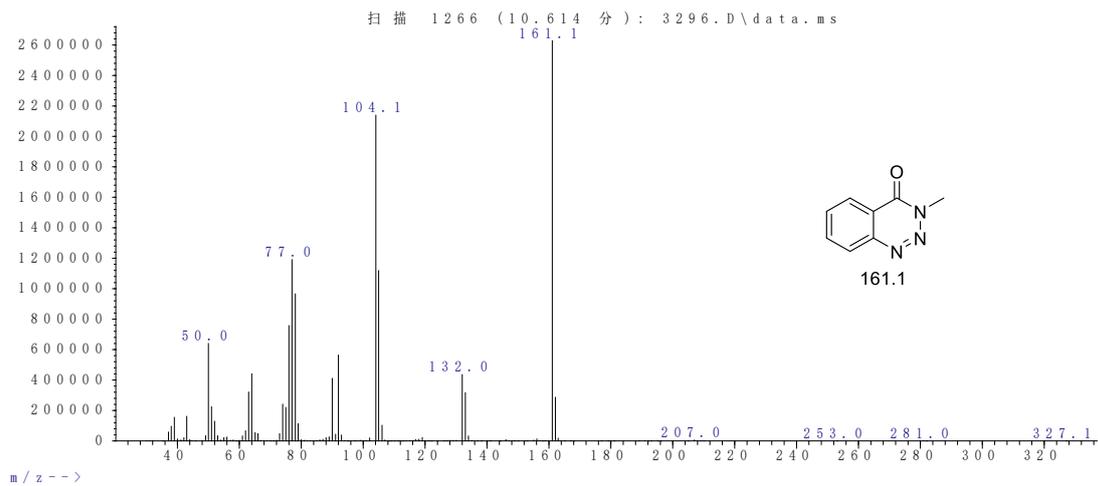
丰度



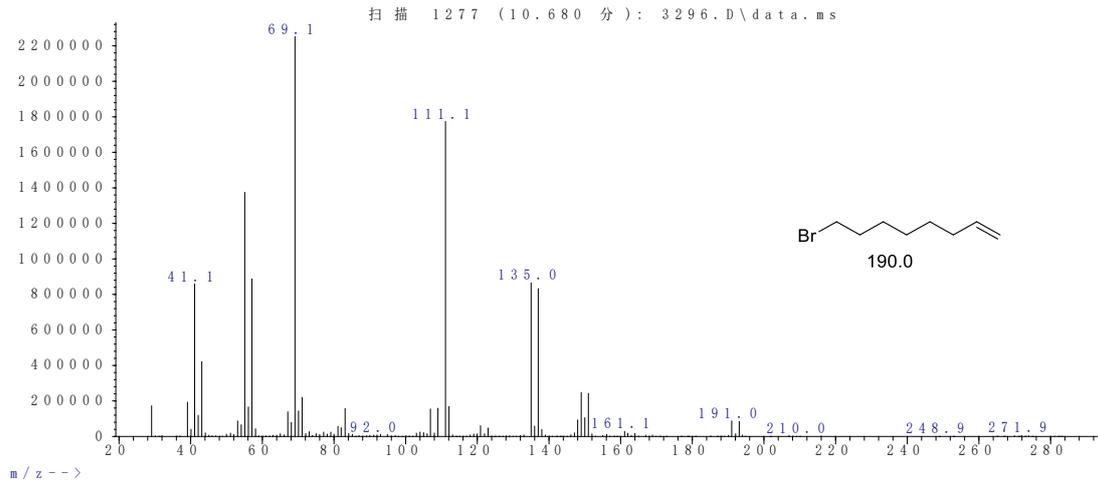
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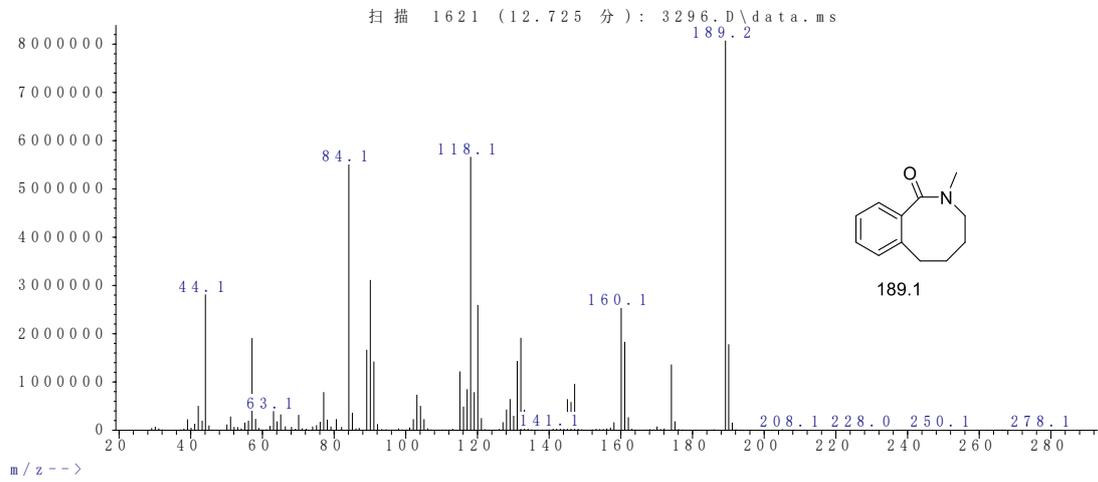
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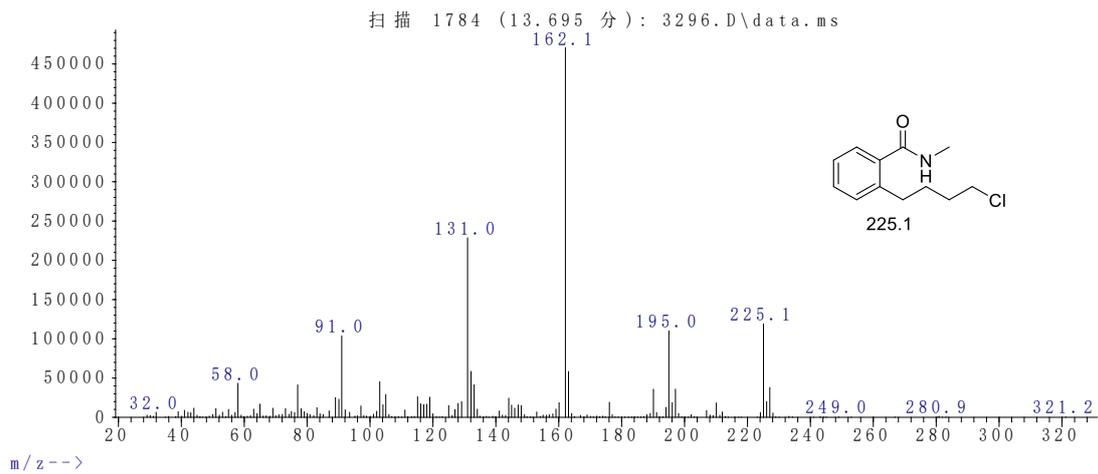
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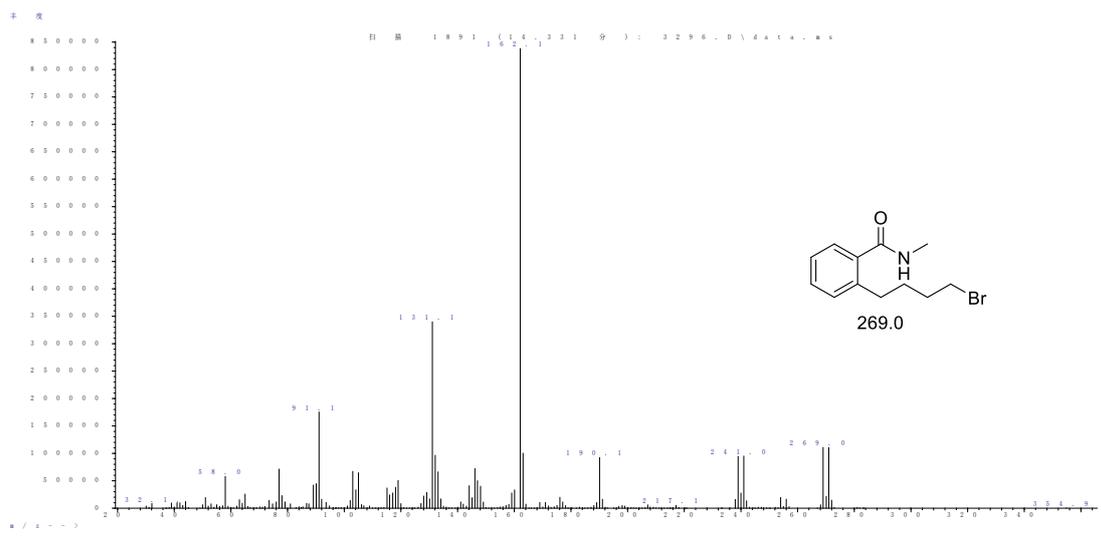


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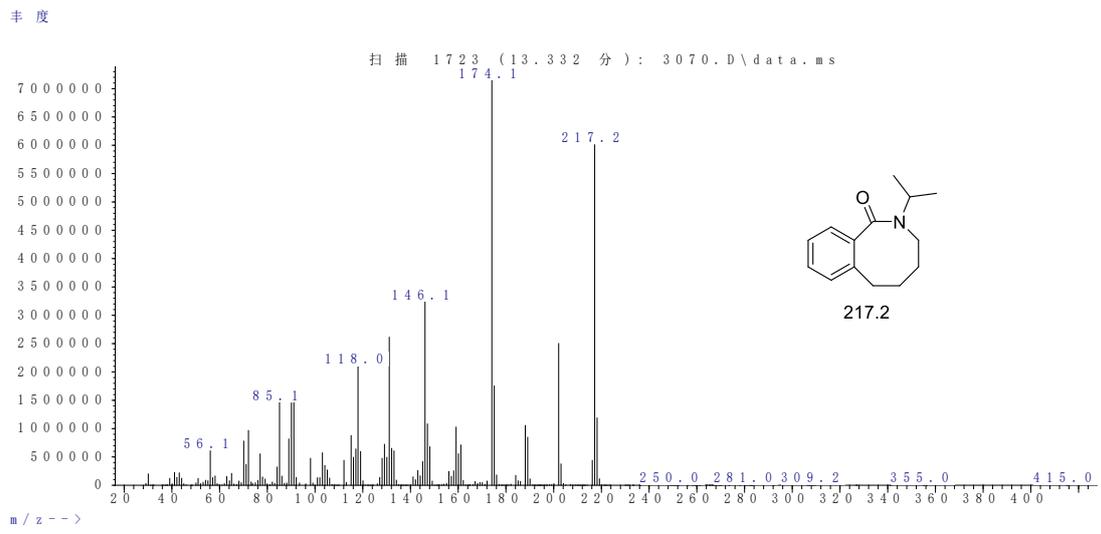
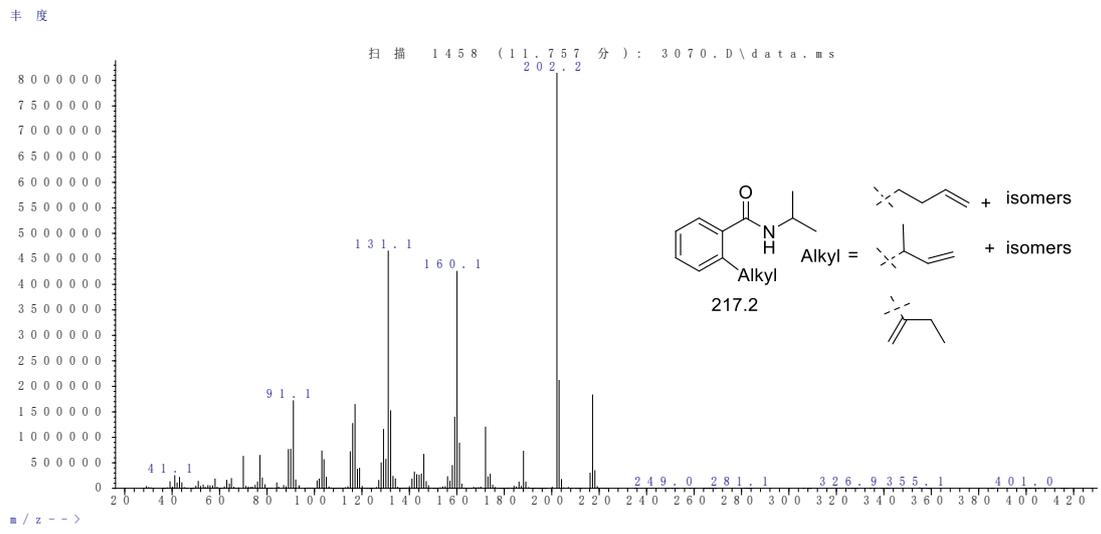
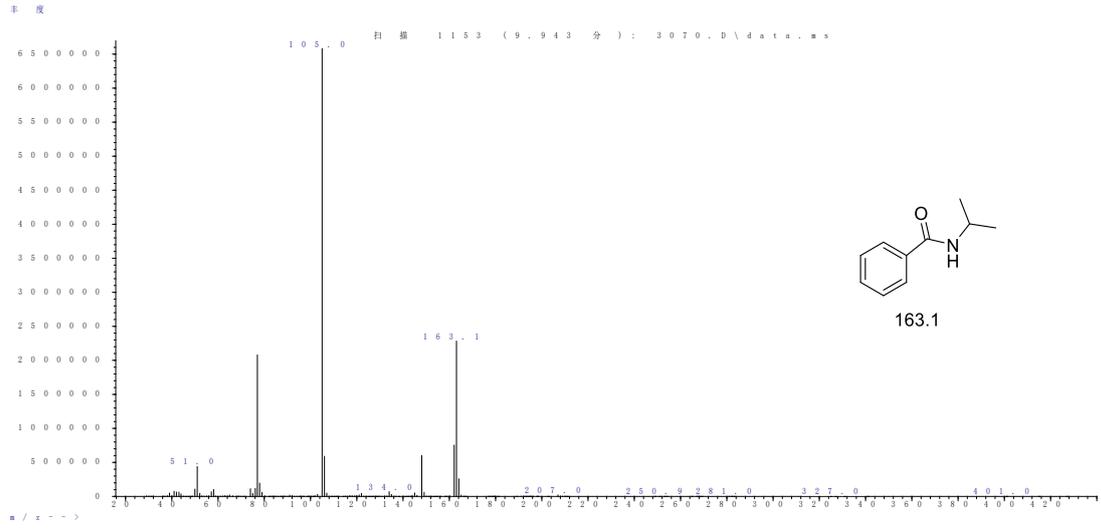


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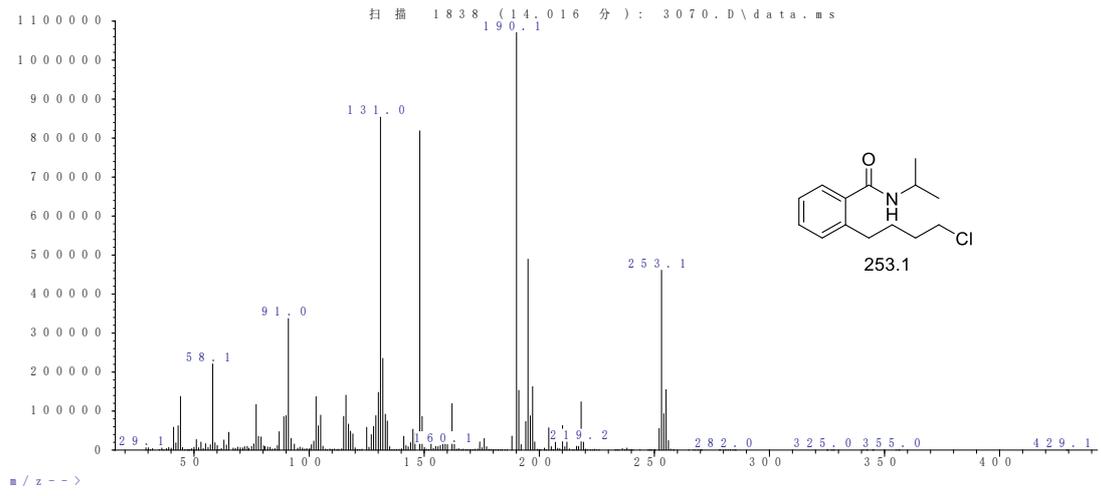




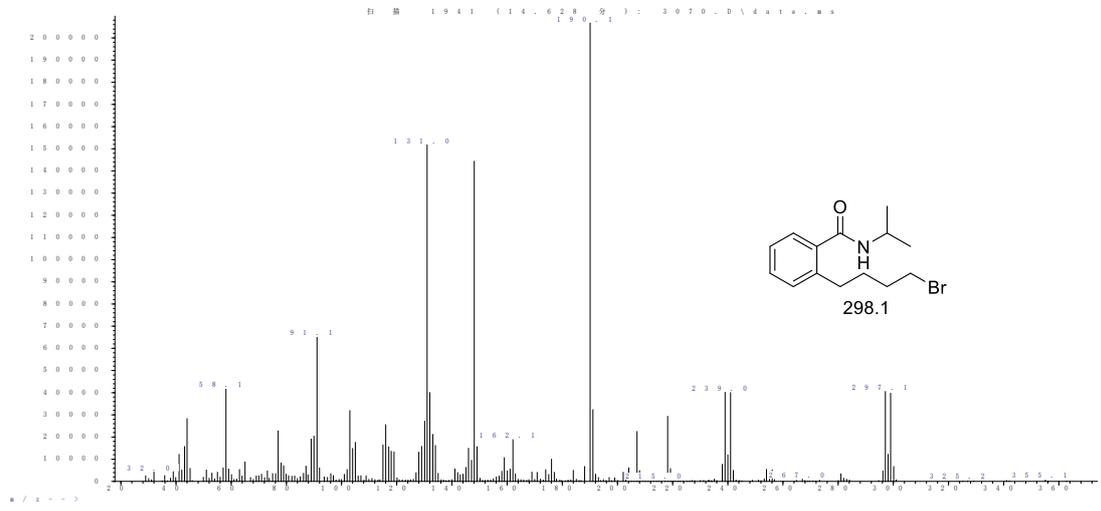




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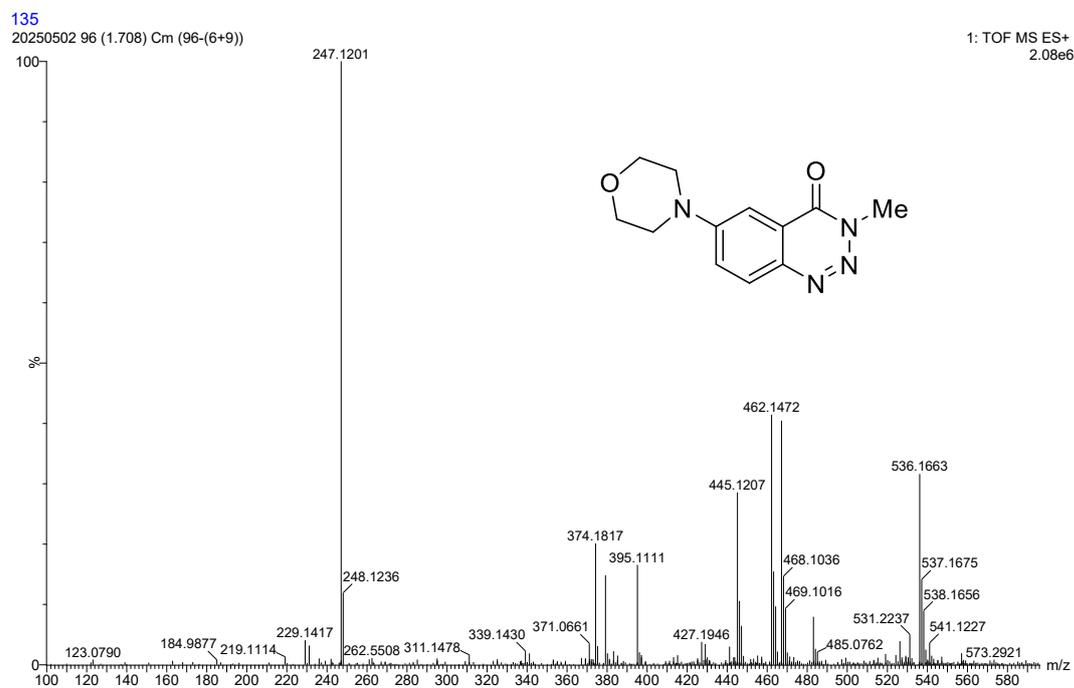


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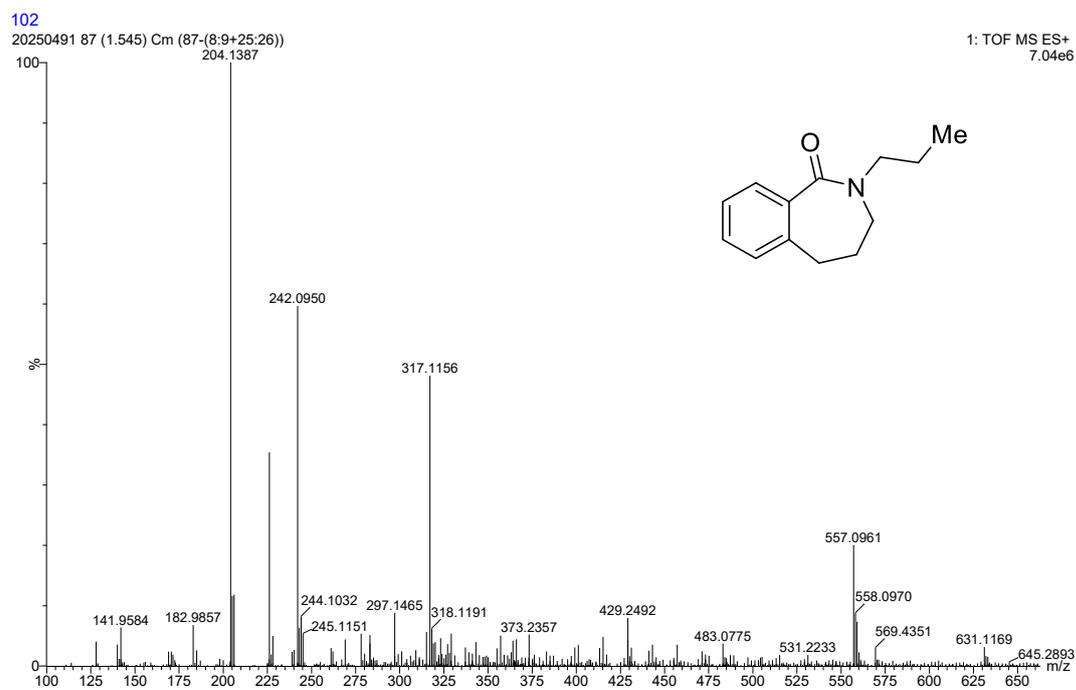


## HRMS of new compounds

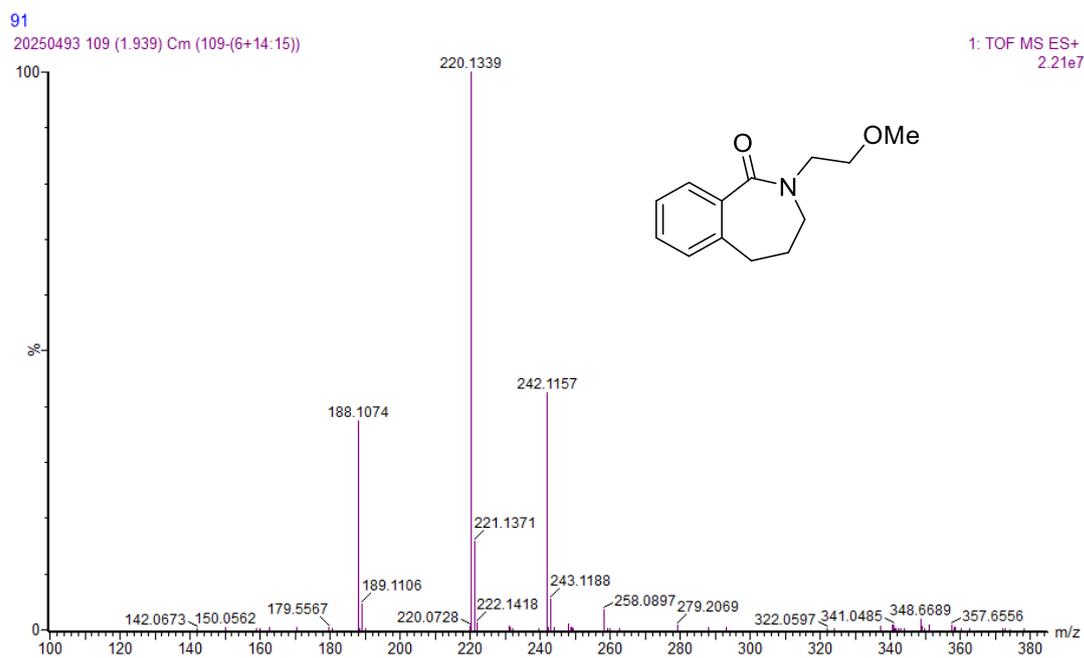
### HRMS of 1r



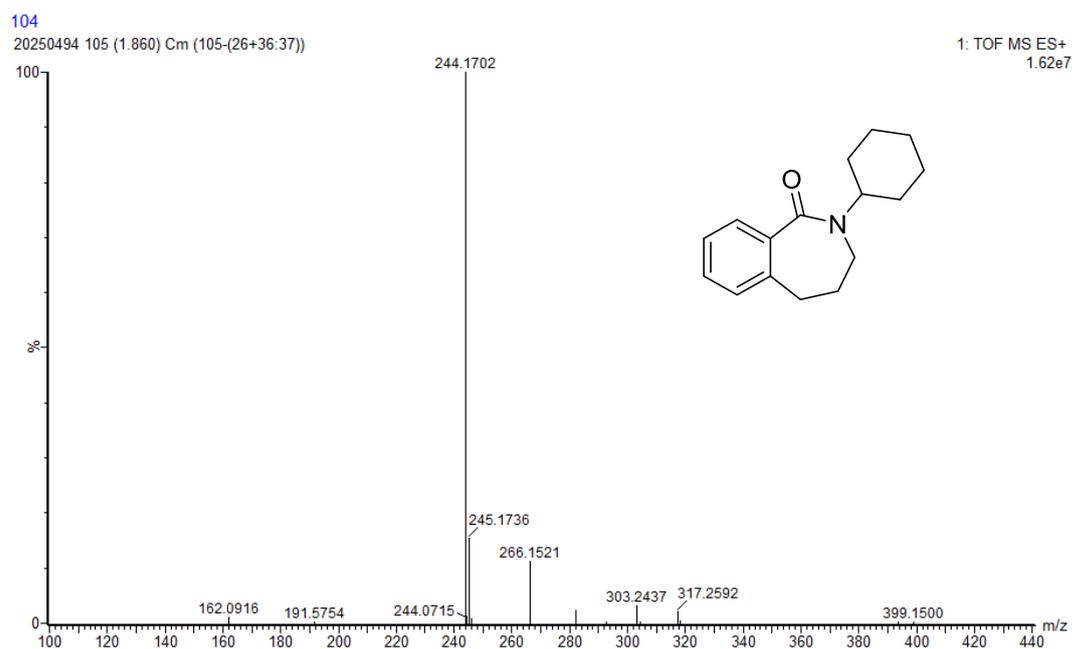
### HRMS of 9ba



## HRMS of 9da



## HRMS of 9ea

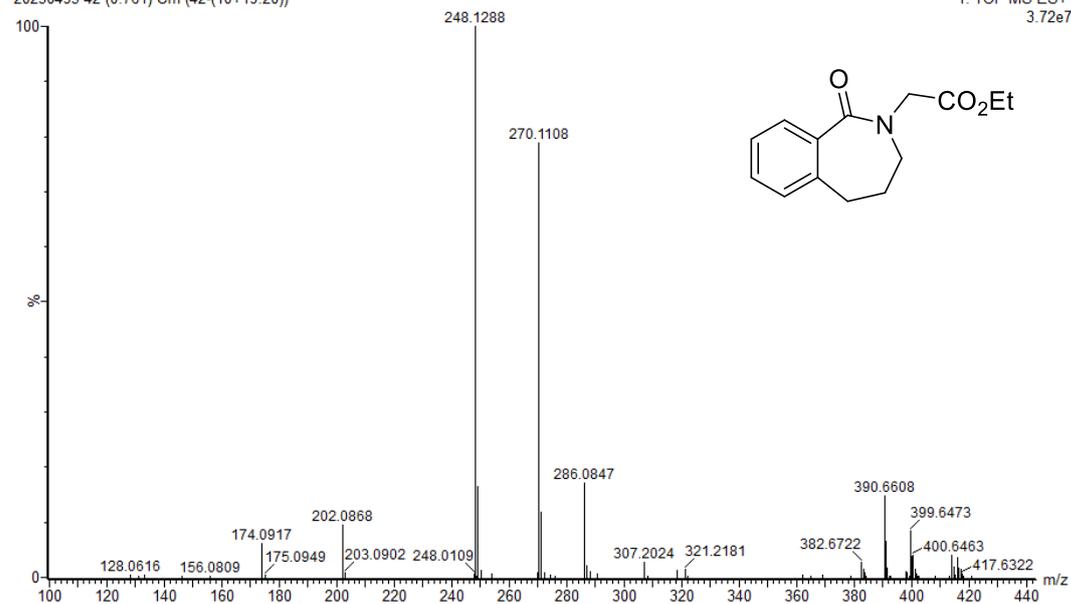


### HRMS of **9fa**

90

20250495 42 (0.761) Cm (42-(10+19.20))

1: TOF MS ES+  
3.72e7

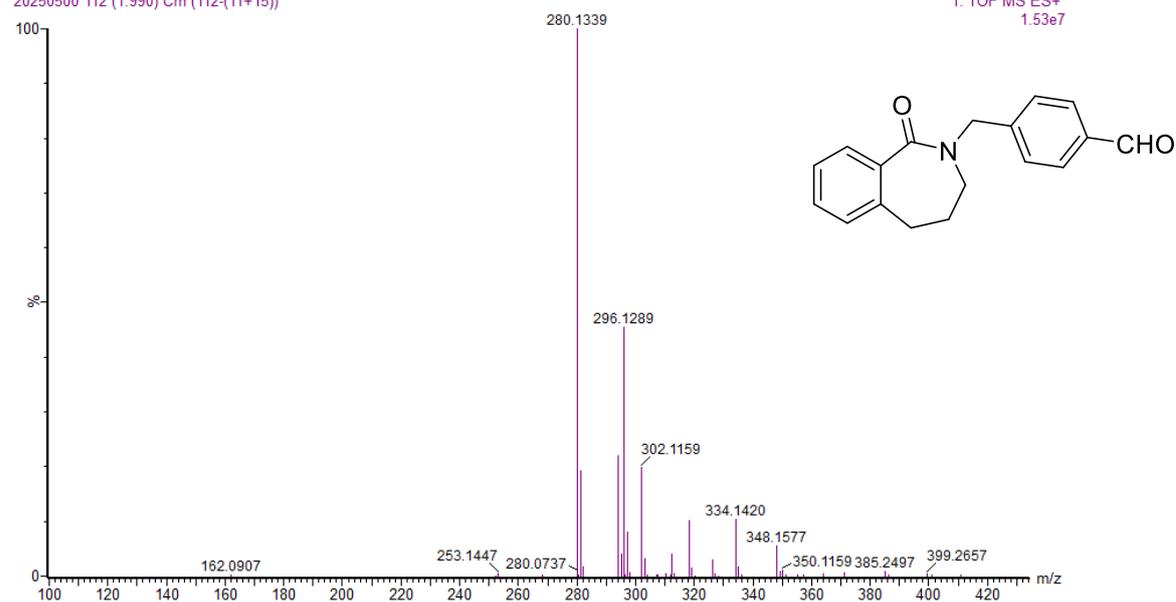


### HRMS of **9ia**

159

20250500 112 (1.990) Cm (112-(11+15))

1: TOF MS ES+  
1.53e7

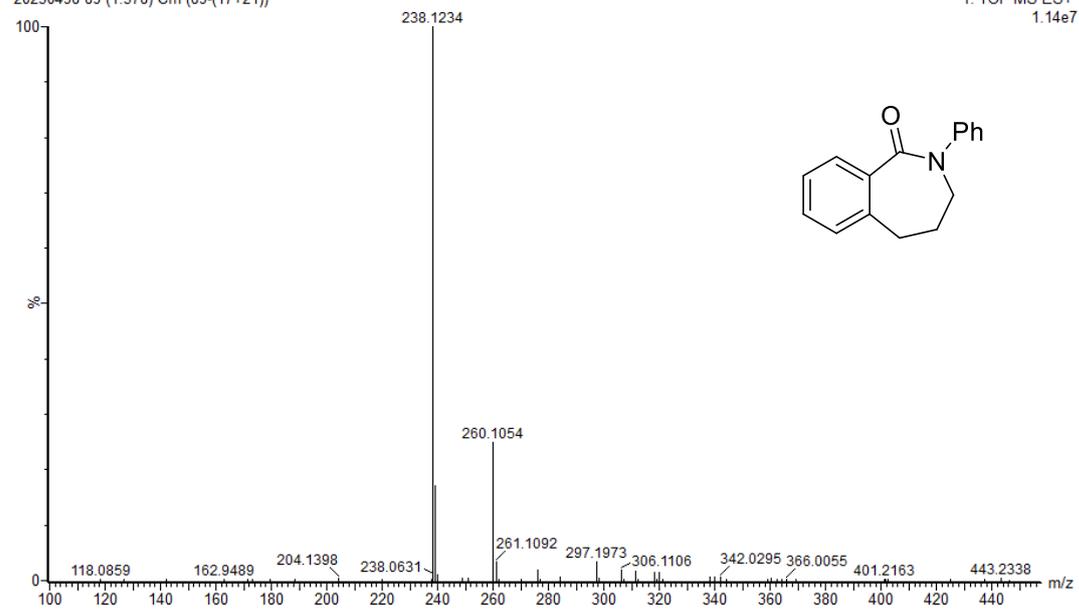


### HRMS of 9ja

95

20250498 89 (1.578) Cm (89-(17+21))

1: TOF MS ES+  
1.14e7

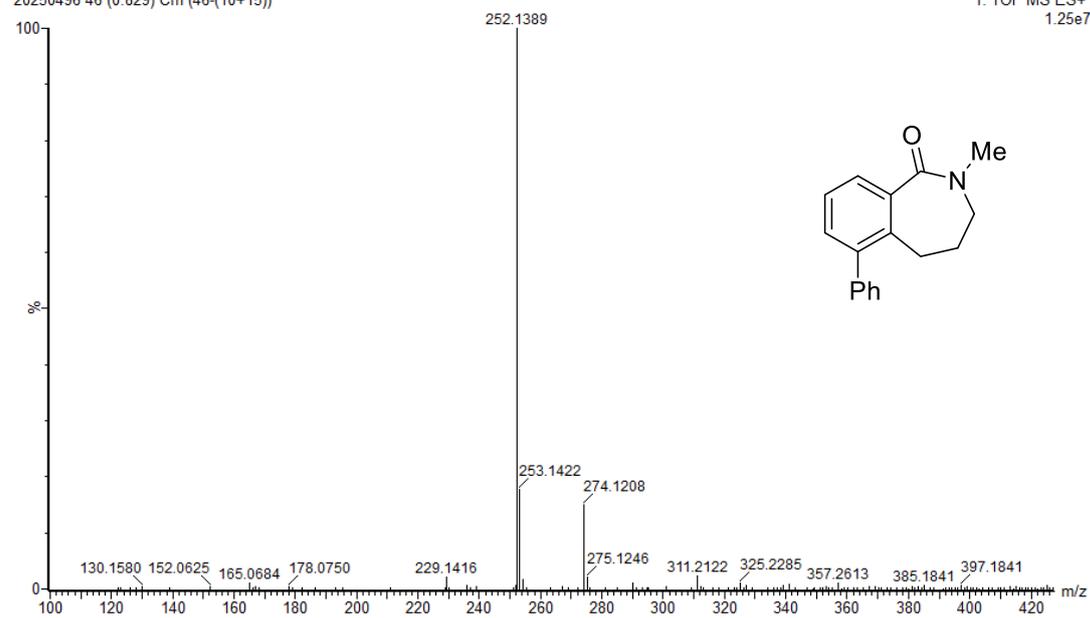


### HRMS of 9ka

109

20250496 46 (0.829) Cm (46-(10+15))

1: TOF MS ES+  
1.25e7

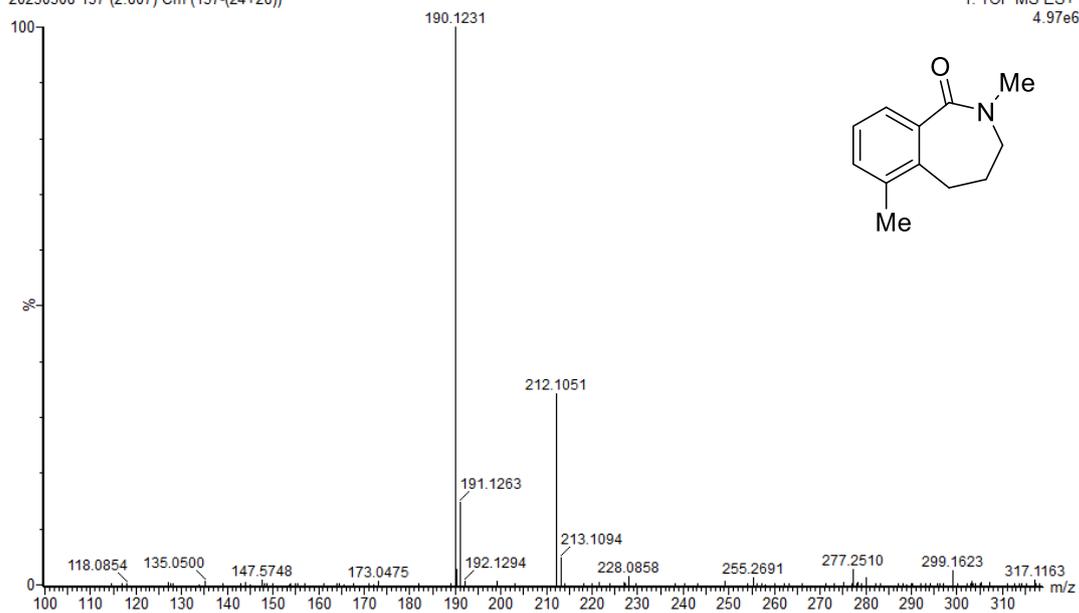


### HRMS of 9la

92

20250508 157 (2.807) Cm (157-(24+28))

1: TOF MS ES+  
4.97e6

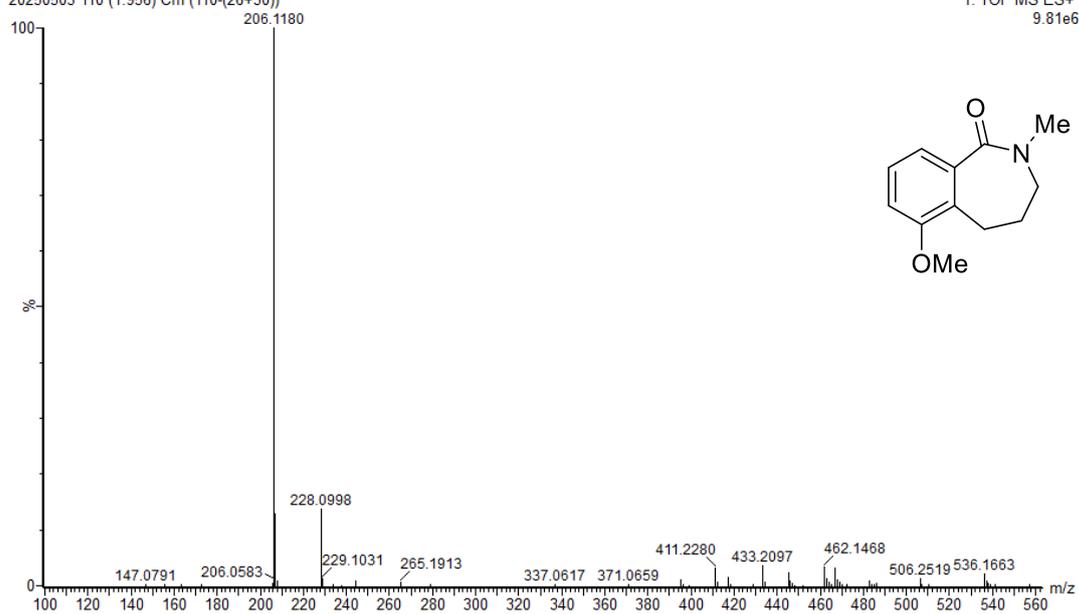


### HRMS of 9ma

111

20250503 110 (1.956) Cm (110-(26+30))

1: TOF MS ES+  
9.81e6

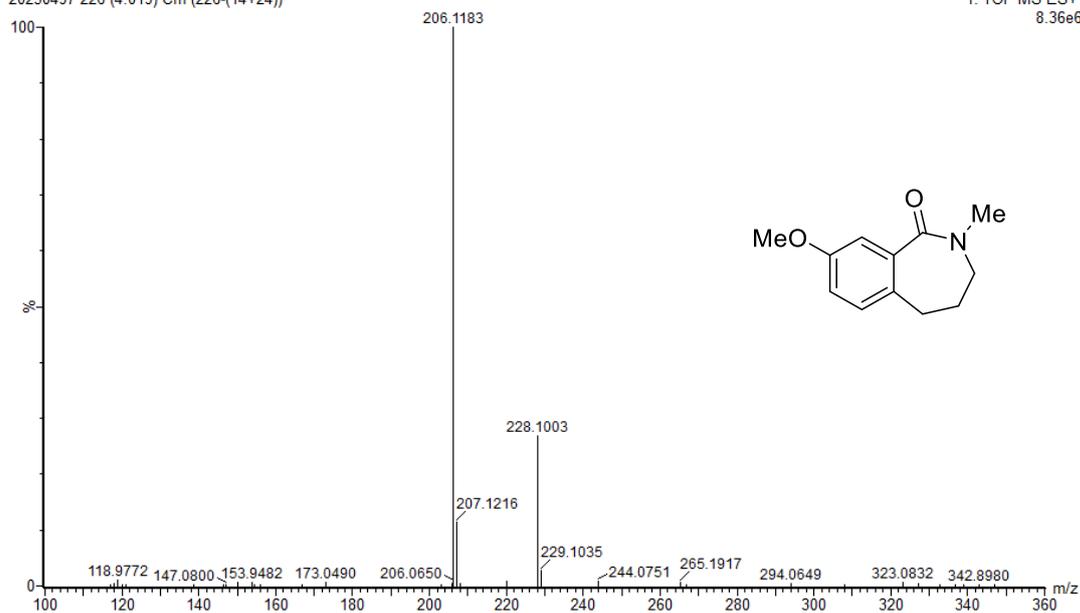


### HRMS of 9oa

106

20250497 226 (4.019) Cm (226-(14+24))

1: TOF MS ES+  
8.36e6

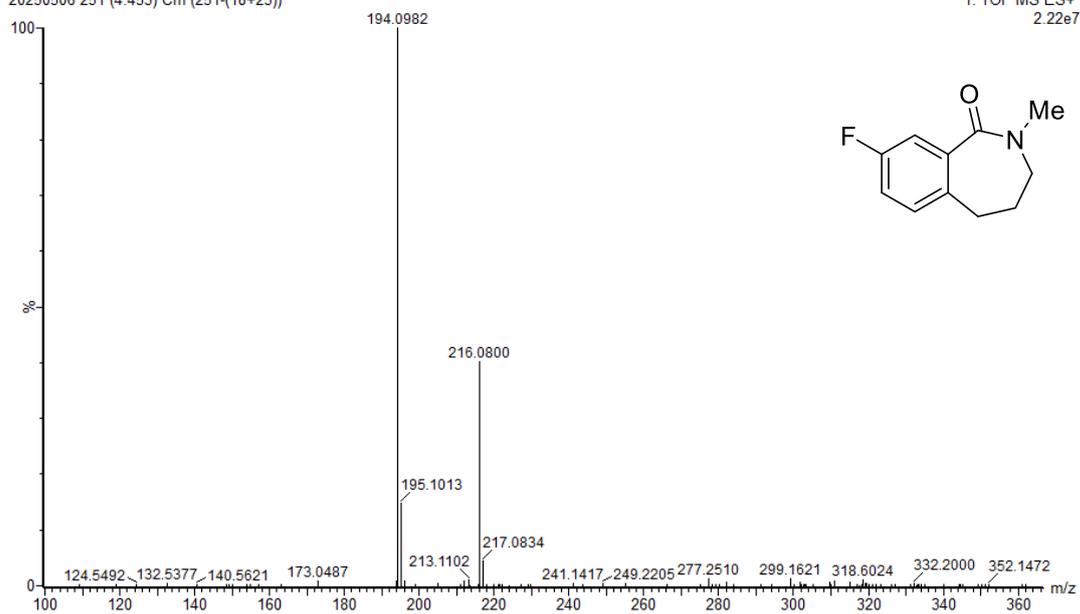


### HRMS of 9pa

114

20250506 251 (4.453) Cm (251-(18+23))

1: TOF MS ES+  
2.22e7

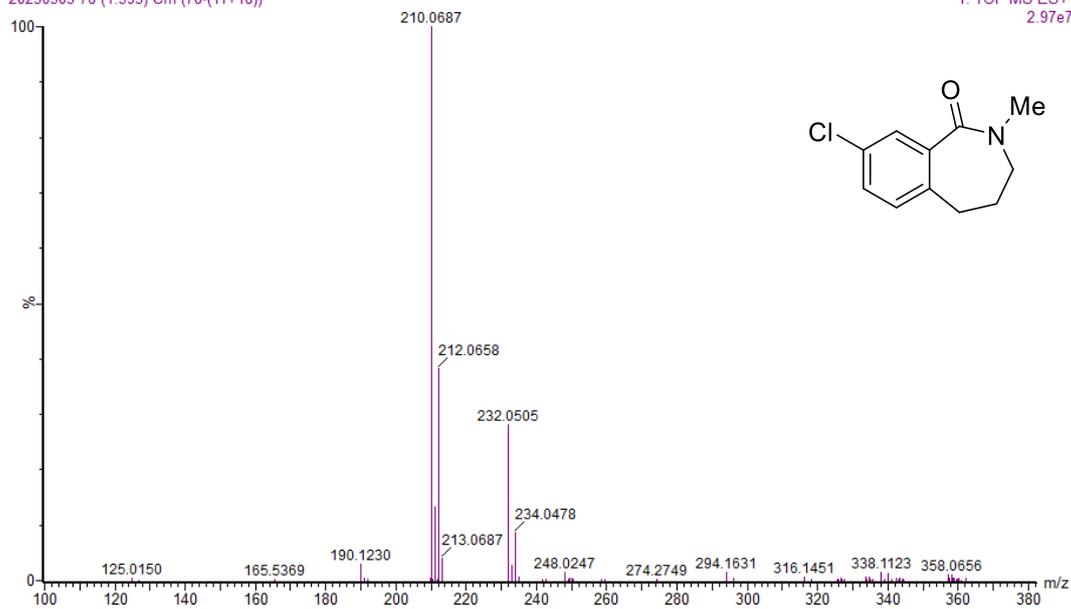


## HRMS of 9qa

115

20250505 78 (1.393) Cm (78-(11+18))

1: TOF MS ES+  
2.97e7

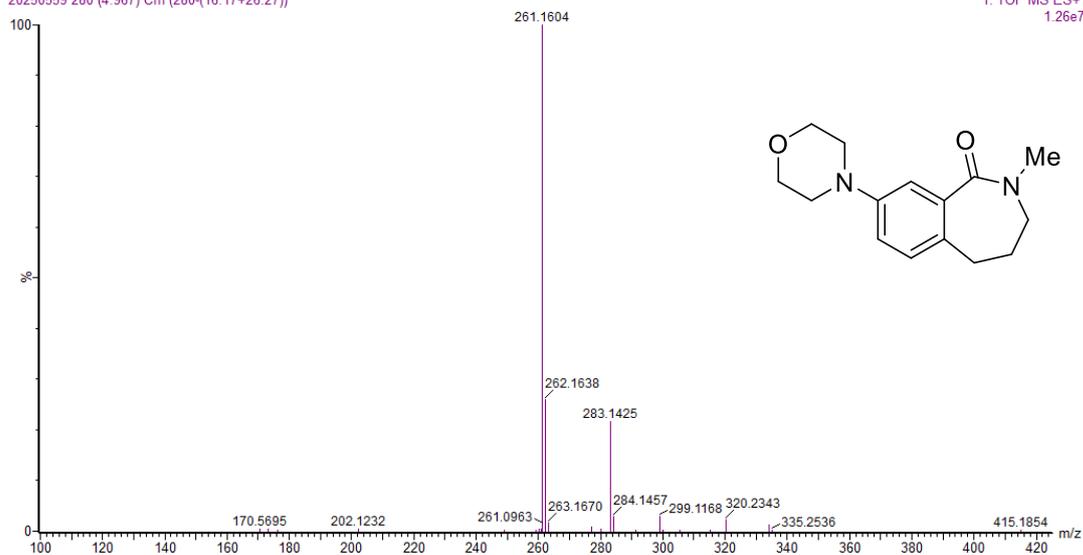


## HRMS of 9ra

D162

20250559 280 (4.967) Cm (280-(16:17+26:27))

1: TOF MS ES+  
1.26e7

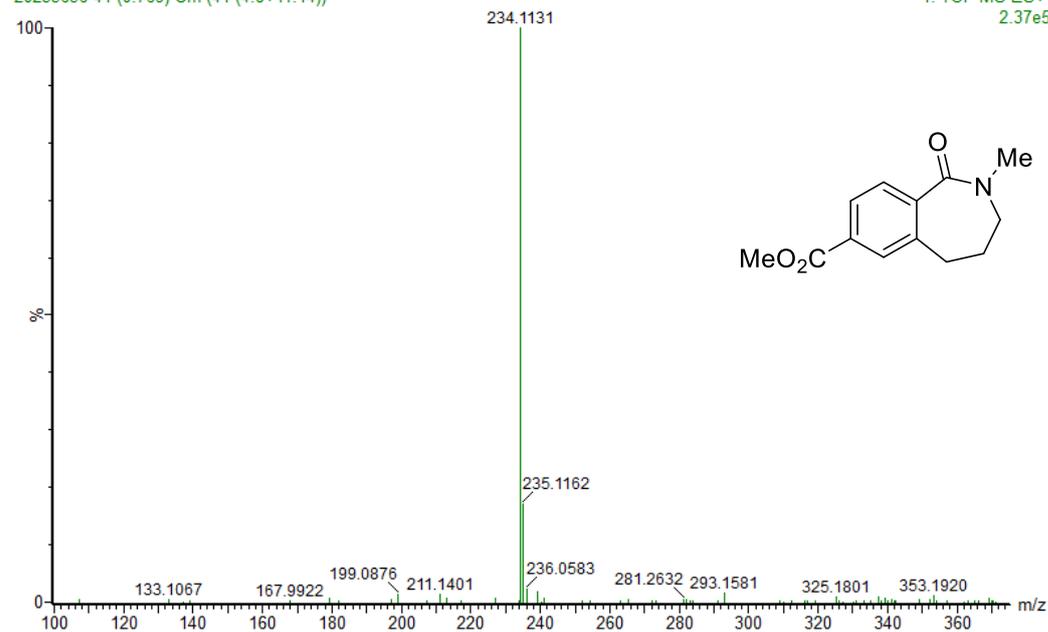


### HRMS of 9sa

D107

20253656 41 (0.769) Cm (41-(4:8+11:14))

1: TOF MS ES+  
2.37e5

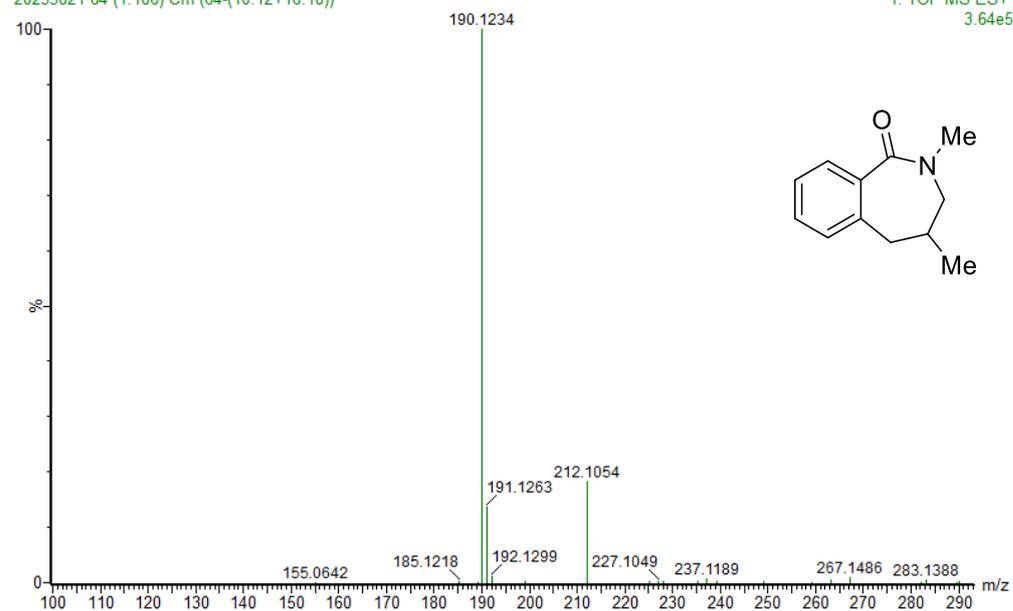


### HRMS of 9af

186

20253821 64 (1.186) Cm (64-(10:12+16:18))

1: TOF MS ES+  
3.64e5

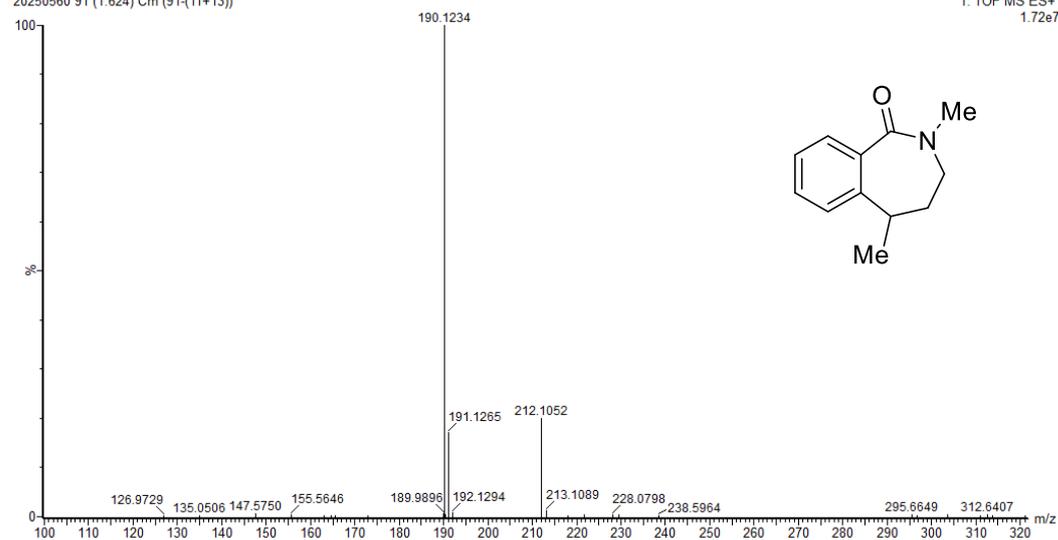


## HRMS of 9ag

D163

20250560 91 (1.624) Cm (91-(11+13))

1: TOF MS ES+  
1.72e7

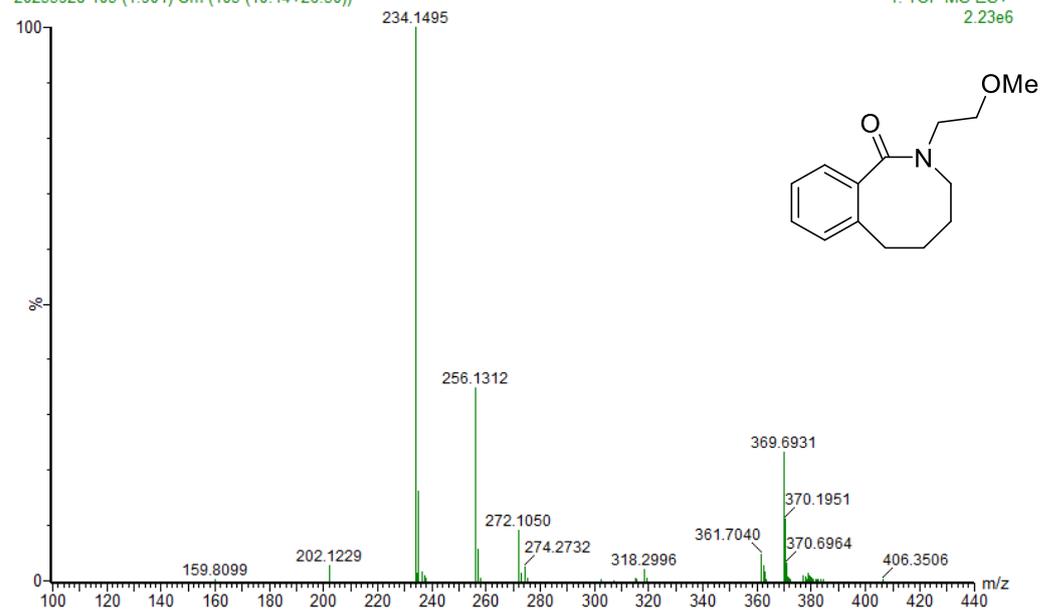


## HRMS of 10da

D202

20253928 103 (1.901) Cm (103-(10:14+26:30))

1: TOF MS ES+  
2.23e6

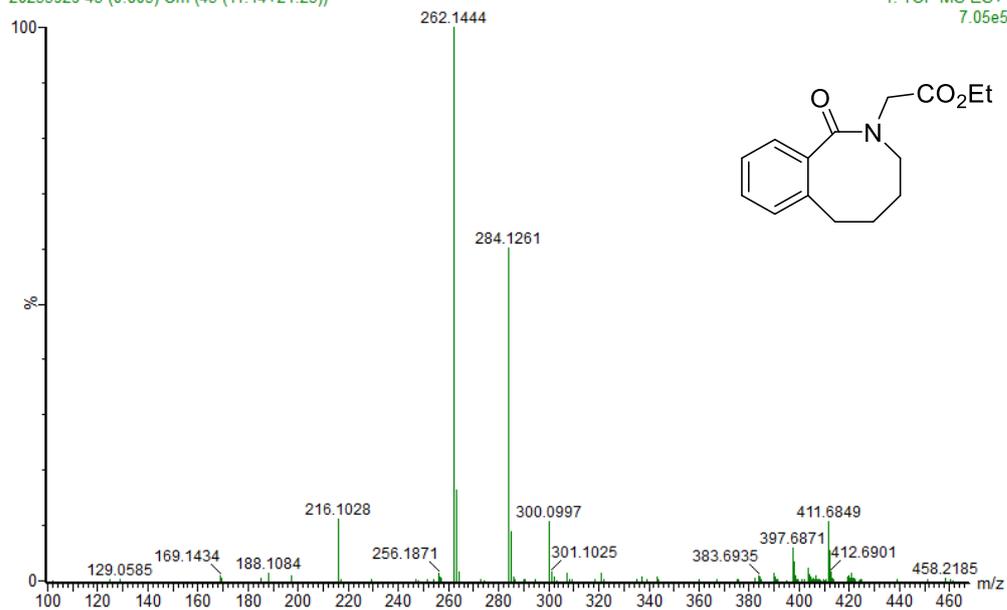


## HRMS of 10fa

D203

20253929 43 (0.803) Cm (43-(11:14+21:23))

1: TOF MS ES+  
7.05e5

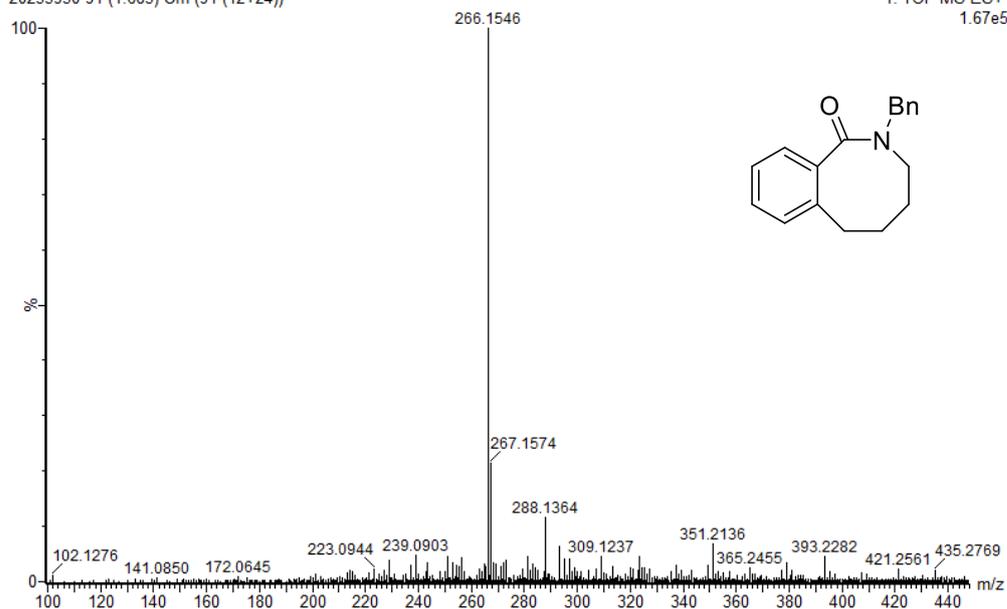


## HRMS of 10ga

D204

20253930 91 (1.683) Cm (91-(12+24))

1: TOF MS ES+  
1.67e5

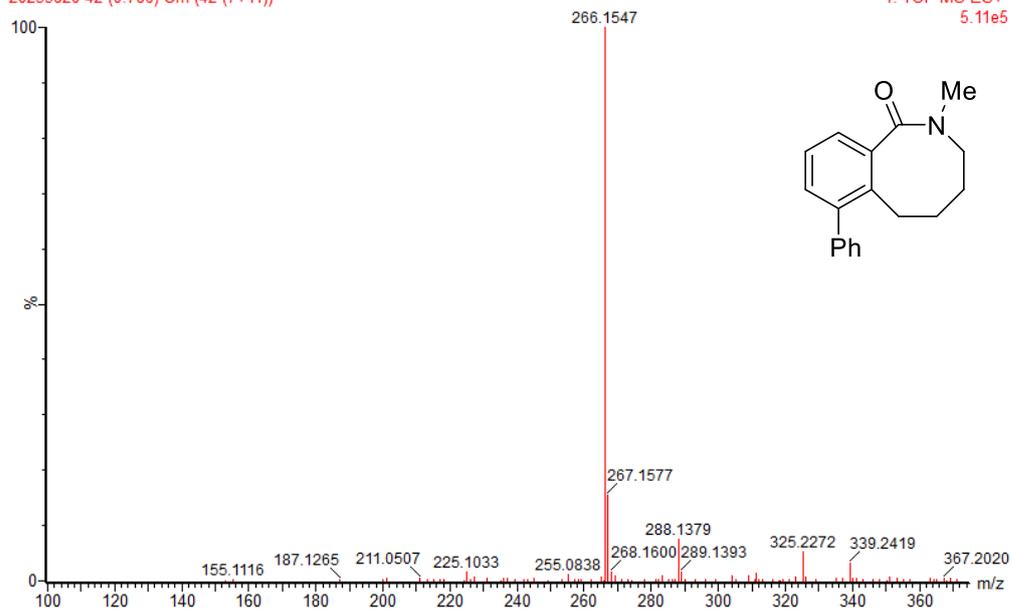


### HRMS of 10ka

188

20253820 42 (0.786) Cm (42-(7+11))

1: TOF MS ES+  
5.11e5

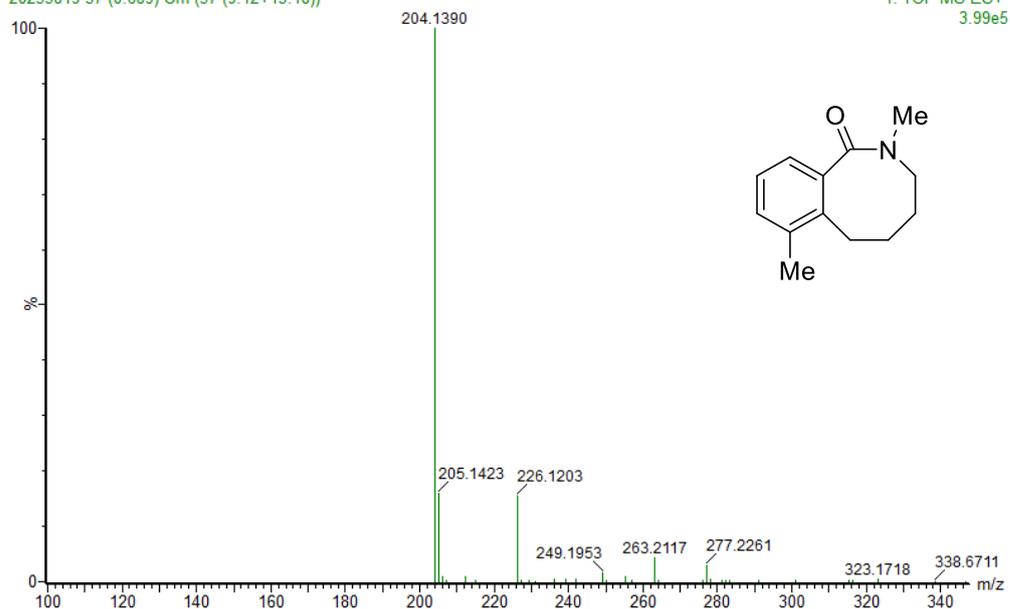


### HRMS of 10la

189

20253819 37 (0.689) Cm (37-(9:12+15:18))

1: TOF MS ES+  
3.99e5

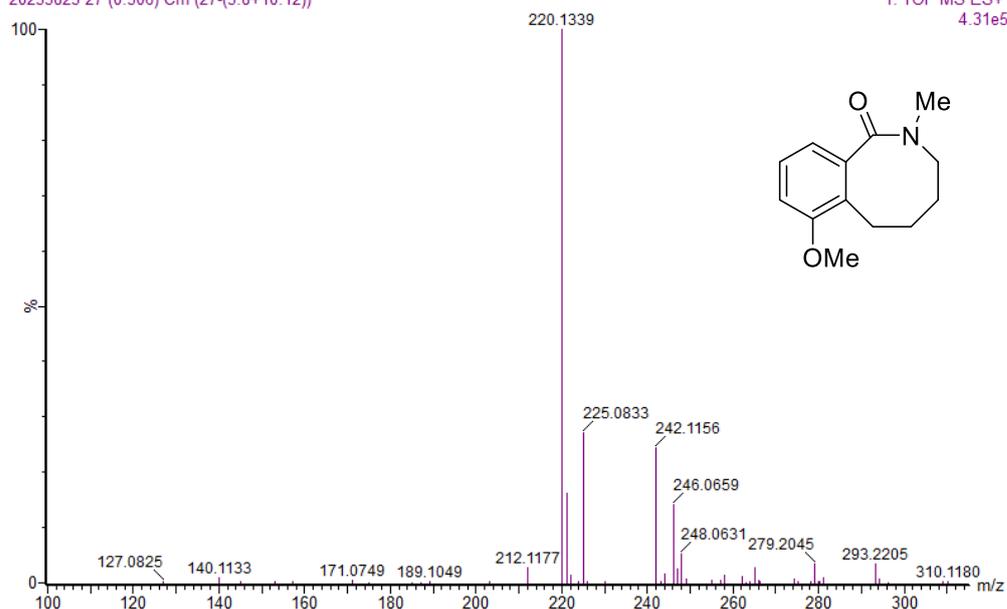


### HRMS of 10ma

193

20253825 27 (0.506) Cm (27-(5:8+10:12))

1: TOF MS ES+  
4.31e5

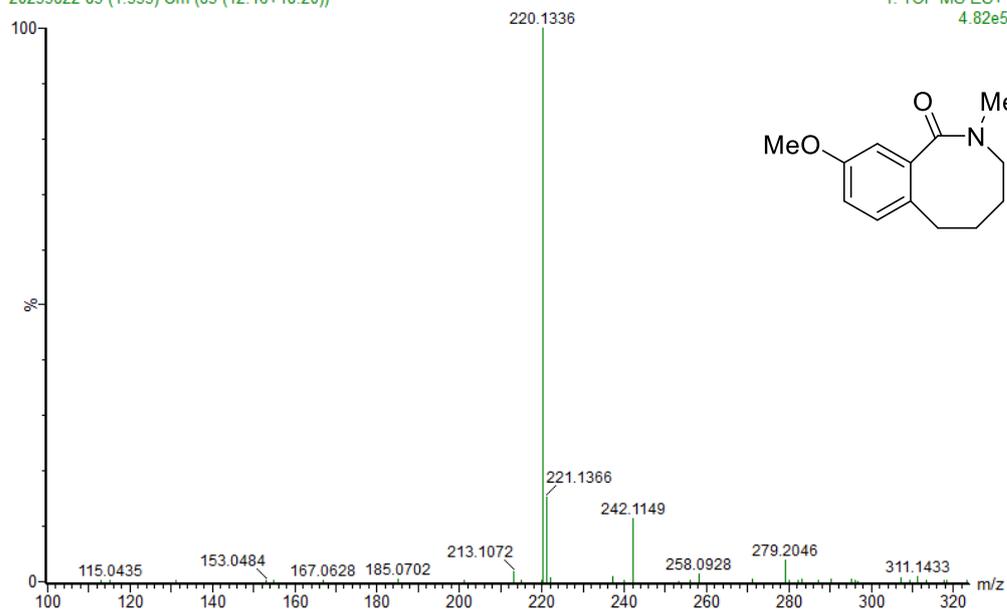


### HRMS of 10oa

190

20253822 83 (1.535) Cm (83-(12:16+18:20))

1: TOF MS ES+  
4.82e5

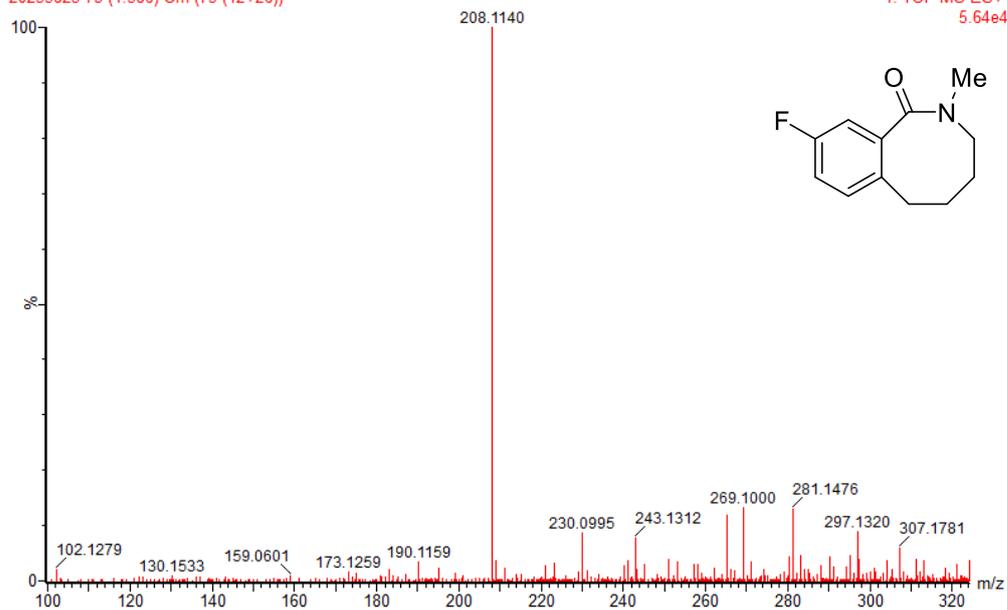


## HRMS of 10pa

191

20253823 75 (1.386) Cm (75-(12+26))

1: TOF MS ES+  
5.64e4

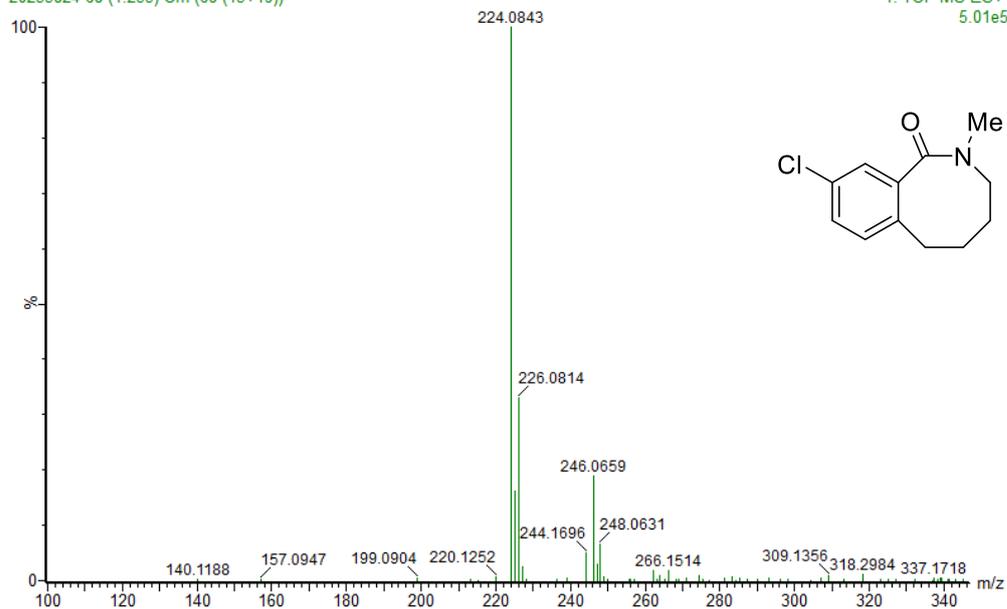


## HRMS of 10qa

192

20253824 68 (1.255) Cm (68-(13+19))

1: TOF MS ES+  
5.01e5



# HRMS of 10sa

D206

20254025 234 (4.330) Cm (234-(13:15+17:20))

1: TOF MS ES+  
2.97e5

