Supporting Information for:

One-pot synthesis of *N*-aryl-3-spirocyclic-*β*-lactams and further regiospecific *β*-lactam ring-opening/recyclization reactions catalyzed by Lewis-Brønsted acids combined superacid catalyst system: A new entry to 3-spirocyclicquinolin-4(1*H*)-ones

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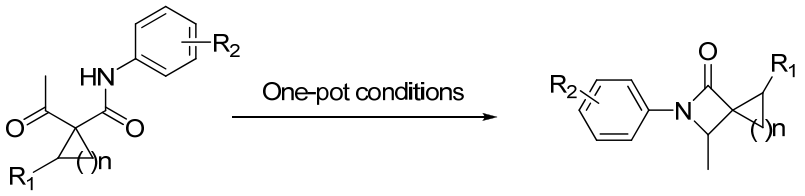
Contents

I. General Information

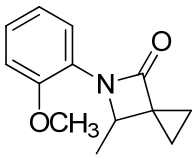
All reagents were purchased from commercial sources and used without treatment, unless otherwise indicated. The products were purified by column chromatography over silica gel. ^{1}H NMR and ^{13}C NMR spectra were recorded at 25 °C at 500 MHz and 125 MHz, respectively, with TMS as internal standard. Mass spectra were recorded on BRUKER AutoflexIII Smartbeam MS-spectrometer. High resolution mass spectra (HRMS) were recorded on Bruck microTof by using ESI method. Infrared spectrum (IR) was measured with FT-IR Microspectrometry (D/MAX-IIIC) using KBr tablet method.

II. Synthesis and analytical data for compounds 2a-2m, 3a-3m and 4a



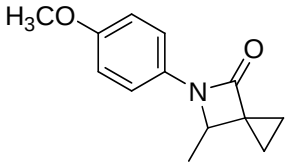
1 2

Synthesis of *N*-aryl-3-spirocyclic-*β*-lactams (with **2a** as an example): To a solution of **1a** (5 mmol, 1.165g) in THF (25 mL), $NaBH_4$ (0.228 g, 6 mmol) was added, and then the reaction mixture was stirred at room temperature until the staring material was consumed (monitored by TLC). Following the addition of KOH (1.4 g, 25 mmol) and *p*-toluenesulfonyl chloride (1.905 g, 10 mmol) into the reaction mixture, the reaction mixture was warmed to 66 ^{o}C and stirred until the reaction complete. Upon cooling to room temperature, the reaction mixture was treated with 50 mL brine, and then extracted with dichloromethane (2 × 20 mL). The combined organic layer was washed with brine (3 × 50 mL), dried over $MgSO_4$ and filtered. The filtrate was concentrated in *vacuum*, and then purified by silica gel column chromatography (petroleum ether : ethyl acetate = 16 : 1) to afford **2a** (0.82 g, 75% yield).



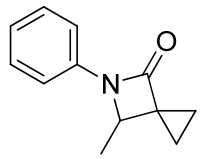
5-(2-methoxyphenyl)-6-methyl-5-azaspiro[2.3]hexan-4-one

(**2a**) White solid, m.p. 80-83 ^{o}C; **^{1}H-NMR** (500 MHz, $CDCl_3$): δ = 0.86-0.90 (m, 1H), 1.02-1.05 (m, 1H), 1.15-1.20 (m, 1H), 1.28-1.32 (m, 1H), 1.25 (d, *J* = 6.5 Hz, 3H), 4.54 (q, *J* = 6.0 Hz, 1H), 3.84 (s, 3H), 6.90-6.93 (m, 1H), 6.95-6-96 (m, 1H), 7.08-7.11 (m, 1H), 7.80-7.82 (m, 1H); **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = 6.9, 8.3, 17.3, 37.8, 55.5, 58.4, 117.4, 121.1, 123.3, 125.2, 125.8, 150.4, 170.9; **IR** (KBr): 2962, 2931, 2907, 2837, 1744, 1513, 1363, 1241, 834. **ESI-MS** *m/z* ($[M + H]^+$) 218.1.



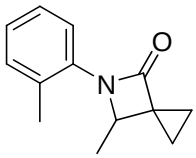
5-(4-methoxyphenyl)-6-methyl-5-azaspiro[2.3]hexan-4-one

(**2b**) White solid, m.p. 83-86 °C; **^{1}H-NMR** (500 MHz, $CDCl_3$): δ = 0.89-0.93 (m, 1H), 1.03-1.07 (m, 1H), 1.15-1.19 (m, 1H), 1.25-1.30 (m, 1H), 1.38 (d, *J* = 6.5 Hz, 3H), 3.78 (s, 3H), 3.19 (q, *J* = 6.0 Hz, 1H), 3.84 (s, 3H), 6.88 (d, *J* = 9.0 Hz, 2H); **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = 6.2, 8.2, 16.4, 37.3, 54.4, 114.4, 117.9, 131.5, 155.6, 169.2; **IR** (KBr): 2967, 2938, 2876, 1728, 1514, 1386, 820; **HRMS** Calcd for $C_{13}H_{16}NO_2$ ($[M + H]^+$) 218.1181; Found 218.1190.



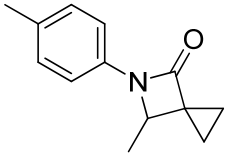
6-methyl-5-phenyl-5-azaspiro[2.3]hexan-4-one

(**2c**) Yellow solid, m.p.22-26 °C; **^{1}H-NMR** (500 MHz, $CDCl_3$): δ = 0.90-0.94 (m, 1H), 1.04-1.08 (m, 1H), 1.15-1.19 (m, 1H), 1.25-1.30 (m, 1H), 1.38 (d, *J* = 6.0 Hz, 3H), 4.21 (q, *J* = 6.0 Hz, 1H), 7.05 (t, *J* = 7.0 Hz, 1H), 7.33 (t, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 7.5 Hz, 2H); **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = 6.4, 8.3, 13.0, 37.2, 54.1, 116.4, 123.0, 129.0, 137.7, 169.7; **IR** (KBr): 2969, 2937, 2880, 1747, 1590, 1521, 1484, 1365, 1148, 755. **ESI-MS** *m/z* ($[M + H]^+$) 188.2.



6-methyl-5-*o*-tolyl-5-azaspiro[2.3]hexan-4-one

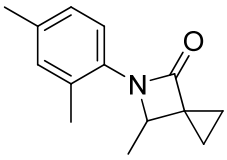
(**2d**) Yellow solid, m.p.45-47 °C; **^{1}H-NMR** (500 MHz, $CDCl_3$): δ = 0.90-0.93 (m, 1H), 1.04-1.08 (m, 1H), 1.12-1.23 (m, 1H), 1.26-1.32 (m, 1H), 1.20 (d, *J* = 6.0 Hz, 3H), 4.31 (q, *J* = 6.0 Hz, 1H), 7.10-7.14 (m, 1H), 7.16-7.18 (m, 1H), 7.19-7.24 (m, 1H); **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = 6.4, 8.0, 16.6, 18.9, 36.8, 123.6, 126.2, 126.3, 131.2, 132.8, 134.8, 170.2; **IR** (KBr): 2967, 2932, 2870, 1753, 1590, 1484, 1360, 1150, 754; **HRMS** Calcd for $C_{13}H_{16}NO$ ($[M + H]^+$) 202.1232; Found 202.1226.



6-methyl-5-*p*-tolyl-5-azaspiro[2.3]hexan-4-one

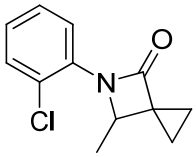
(**2e**) White solid, m.p.56-58 °C; **^{1}H-NMR** (500 MHz, $CDCl_3$): δ = 0.90-0.93 (m, 1H), 1.04-1.08 (m, 1H), 1.16-1.28 (m, 1H), 1.29-1.31 (m, 1H), 1.39 (d, *J* = 6.0 Hz, 3H),

4.21 (q, *J* = 6.0 Hz, 1H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.26-7.30 (m, 2H); **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = 6.4, 8.3, 16.4, 20.8, 37.3, 54.2, 116.5, 129.6, 132.7, 135.5, 169.6; **IR** (KBr): 2970, 2928, 2871, 1746, 1598, 1501, 1370, 1147, 756, 694. **ESI-MS** *m/z* ($[M + H]^+$) 202.2.



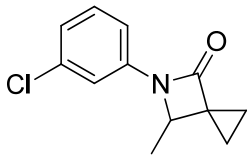
5-(2,4-dimethylphenyl)-6-methyl-5-azaspiro[2.3]hexan-4-one

(**2f**) White solid, m.p.45-47 °C; **^{1}H-NMR** (500 MHz, $CDCl_3$): δ = 0.88-0.93 (m, 1H), 1.03-1.07 (m, 1H), 1.14-1.18 (m, 1H), 1.26-1.31 (m, 1H), 1.19 (d, *J* = 6.5 Hz, 3H), 2.29 (s, 3H), 2.32 (s, 3H), 4.26 (q, *J* = 6.0 Hz, 1H), 6.98 (d, *J* = 8.0 Hz, 1H), 7.02 (s, 1H), 7.10 (d, *J* = 8.0 Hz, 1H); **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = 6.2, 7.8, 16.5, 18.7, 20.7, 36.7, 56.6, 123.7, 126.8, 131.7, 132.2, 132.8, 135.9, 170.1; **IR** (KBr): 2970, 2927, 2868, 1752, 1599, 1503, 1394, 1361, 1136, 979, 759, 693; **HRMS** Calcd for $C_{14}H_{18}NO$ ($[M + H]^+$) 216.1388; Found 216.1391.



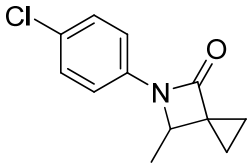
5-(2-chlorophenyl)-6-methyl-5-azaspiro[2.3]hexan-4-one

(**2g**) Pale yellow solid, m.p.84-86 °C; **^{1}H-NMR** (500 MHz, $CDCl_3$): δ = 0.92-0.96 (m, 1H), 1.08-1.12 (m, 1H), 1.19-1.22 (m, 1H), 1.32-1.37 (m, 1H), 1.27 (d, *J* = 3.5 Hz, 3H), 4.70 (q, *J* = 6.0 Hz, 1H), 7.08-7.12 (m, 1H), 7.23-7.27 (m, 1H), 7.35-7.37 (m, 1H), 7.75-7.78 (m, 1H); **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = 7.2, 8.7, 17.0, 37.7, 58.3, 125.3, 125.4, 126.2, 127.4, 130.6, 133.5, 171.3; **IR** (KBr): 2966, 2923, 2865, 1750, 1506, 1358, 12419, 978, 815. **ESI-MS** *m/z* ($[M + H]^+$) 222.1.



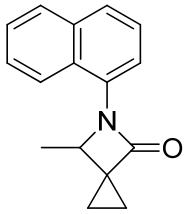
5-(3-chlorophenyl)-6-methyl-5-azaspiro[2.3]hexan-4-one

(**2h**) White liquid; **^{1}H-NMR** (500 MHz, $CDCl_3$): δ = 0.93-0.97 (m, 1H), 1.08-1.12 (m, 1H), 1.19-1.23 (m, 1H), 1.29-1.34 (m, 1H), 1.41 (d, *J* = 6.5 Hz, 3H), 4.22 (q, *J* = 6.0 Hz, 1H), 7.03 (q, *J* = 5.0 Hz, 1H), 7.23-7.30 (m, 2H), 7.37 (d, *J* = 2.0 Hz, 1H); **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = 6.7, 8.6, 16.3, 37.4, 54.4, 144.5, 116.4, 123.0, 130.0, 134.7, 138.7; **IR** (KBr): 2972, 2926, 1755, 1594, 1486, 1356, 1135, 982, 775, 685. **ESI-MS** *m/z* ($[M + H]^+$) 222.1.



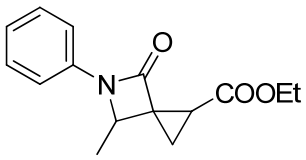
5-(4-chlorophenyl)-6-methyl-5-azaspiro[2.3]hexan-4-one

(**2i**) White solid, m.p.84-87 °C; **^{1}H-NMR** (500 MHz, $CDCl_3$): δ = 0.92-0.97 (m, 1H), 1.07-1.11 (m, 1H), 1.17-1.22 (m, 1H), 1.26-1.31 (m, 1H), 1.32 (d, *J* = 5.0 Hz, 3H), 4.21 (q, *J* = 6.0 Hz, 1H), 3.84 (s, 3H), 7.27-7.34 (m, 4H); **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = 6.7, 8.7, 16.4, 37.6, 54.5, 117.7, 128.1, 129.2, 136.5, 169.9; **IR** (KBr): 2964, 2925, 2866, 1753, 1591, 1485, 1355, 1176, 978, 756; **HRMS** Calcd for $C_{12}H_{13}ClNO$ ($[M + H]^+$) 222.0686; Found 222.0677.



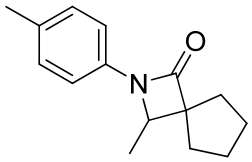
6-methyl-5-(naphthalen-1-yl)-5-azaspiro[2.3]hexan-4-one

(**2j**) Yellow solid, m.p.98-100 °C; **^{1}H-NMR** (500 MHz, $CDCl_3$): δ = 0.98-1.01 (m, 1H), 1.11-1.14 (m, 1H), 1.23 (d, *J* = 6.5 Hz, 3H), 1.25-1.30 (m, 1H), 1.36-1.39 (m, 1H), 4.50 (q, *J* = 6.0 Hz, 1H), 6.98 (d, *J* = 7.5 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.47-7.56 (m, 2H), 7.72 (d, *J* = 8.5 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 8.13 (d, *J* = 8.5 Hz, 1H); **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = 6.7, 8.3, 16.3, 36.8, 57.2, 120.4, 123.7, 125.3, 126.1, 126.2, 126.7, 128.1, 128.4, 132.6, 134.3, 171.1; **IR** (KBr): 2970, 1714, 1409, 1355, 1138, 974, 803, 771. **ESI-MS** *m/z* ($[M + H]^+$) 238.3.



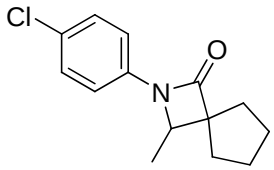
ethyl 4-methyl-6-oxo-5-phenyl-5-azaspiro[2.3]hexane-1-carboxylate

(**2k**) White solid, m.p.78-81 °C; **^{1}H-NMR** (500 MHz, $CDCl_3$): δ = 1.30 (t, *J* = 7.0 Hz, 3H), 1.38 (d, *J* = 6.0 Hz, 3H), 1.61 (q, *J* = 5.0 Hz, 2H), 2.39 (t, *J* = 6.0 Hz, 2H), 2.39 (q, *J* = 6.0 Hz, 1H), 4.15-4.20 (m, 1H), 4.21-4.25 (m, 1H), 4.50 (q, *J* = 6.0 Hz, 1H), 7.08 (t, *J* = 7.0 Hz, 1H), 7.32-7.38 (m, 4H); **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = 13.9, 14.0, 15.2, 21.1, 43.7, 55.3, 61.1, 116.9, 123.7, 129.2, 137.0, 166.5, 170.1; **IR** (KBr): 2982, 2934, 1753, 1716, 1502, 1385, 1314, 1207, 1181, 1001, 758, 693. **ESI-MS** *m/z* ($[M + H]^+$) 260.3.



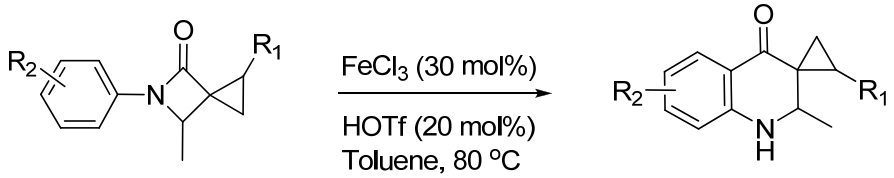
3-methyl-2-*p*-tolyl-2-azaspiro[3.4]octan-1-one

(**2l**) White solid, m.p.83-86 °C; **^{1}H-NMR** (500 MHz, $CDCl_3$): δ = 1.39 (d, *J* = 6.0 Hz, 3H), 1.61-1.69 (m, 2H), 1.81-1.95 (m, 5H), 2.09-2.15 (m, 1H), 2.30 (s, 3H), 3.92 (q, *J* = 6.0 Hz, 1H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H); **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = 15.2, 20.8, 25.1, 25.4, 27.6, 34.2, 58.6, 62.5, 116.9, 129.5, 132.9, 135.1, 171.3; **IR** (KBr): 2973, 1738, 1507, 1357, 1290, 1253, 1146, 1047, 977, 761. **ESI-MS** *m/z* ($[M + H]^+$) 230.2.



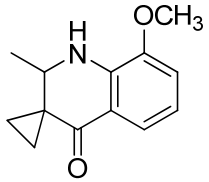
2-(4-chlorophenyl)-3-methyl-2-azaspiro[3.4]octan-1-one

(**2m**) White solid, m.p.112-115 °C; **^{1}H-NMR** (500 MHz, $CDCl_3$): δ = 1.39 (d, *J* = 6.0 Hz, 3H), 1.62-1.68 (m, 2H), 1.80-1.95 (m, 5H), 2.12-2.16 (m, 1H), 3.94 (q, *J* = 6.0 Hz, 1H), 7.27-7.33 (m, 4H); **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = 15.2, 25.1, 25.4, 27.6, 34.3, 58.7, 62.9, 118.1, 128.3, 129.1, 136.1, 171.5; **IR** (KBr): 2976, 1750, 1599, 1355, 1119, 978, 802, 763. **ESI-MS** *m/z* ($[M + H]^+$) 250.1.



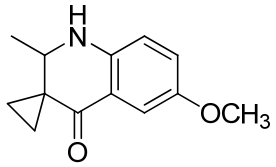
2 3

Synthesis of 3-spirocyclicquiolin-4(1*H*)-ones (with **3a** as an example): To a solution of **2a** (217 mg, 1 mmol) in anhydrous toluene (5 mL), $FeCl_3$ (0.048 g, 0.3 mmol) and TfOH (18 μl, 0.2 mmol) were added in succession. The mixture was warmed to 80 °C and stirred until **2a** disappeared (monitored by TLC). Upon cooling to room temperature, the solvent was directly evaporated in vacuum, and then purified the product by silica gel column chromatography (petroleum ether : ethyl acetate = 20 : 1) to give **3a** (198 mg, 91% yield).



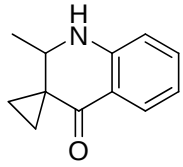
8'-methoxy-2'-methyl-1'*H*-spiro[cyclopropane-1,3'-quinolin]-4'(2'*H*)-one

(**3a**) White solid, m.p.100-102 °C; **^{1}H-NMR** (500 MHz, $CDCl_3$): δ = 0.84-0.94 (m, 2H), 1.21 (d, *J* = 7.0 Hz, 3H), 1.23-1.26 (m, 1H), 1.37-1.40 (m, 1H), 3.48 (q, *J* = 6.5 Hz, 1H), 3.87 (s, 3H), 4.8 (s, 1H), 6.66 (t, *J* = 8.0 Hz, 1H), 6.5 (q, *J* = 6.5 Hz, 1H), 7.45 (q, *J* = 6.5 Hz, 1H); **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = 11.2, 15.8, 17.8, 31.1, 52.9, 55.6, 113.4, 116.2, 118.7, 118.7, 141.5, 147.2, 194.3; **IR** (KBr): 3422, 3313, 3013, 2930, 2838, 1649, 1611, 1508, 1322, 1254, 1221, 1035, 999, 745, 621; **HRMS** Calcd for $C_{13}H_{16}NO_2$ ($[M + H]^+$) 218.1181; Found 218.1186.



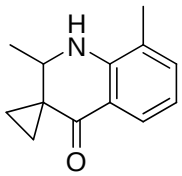
6'-methoxy-2'-methyl-1'*H*-spiro[cyclopropane-1,3'-quinolin]-4'(2'*H*)-one

(**3b**) White solid, m.p.126-128 °C; **^{1}H-NMR** (500 MHz, $CDCl_3$): δ = 0.86-0.93 (m, 2H), 1.19 (d, *J* = 6.5 Hz, 3H), 1.25-1.29 (m, 1H), 1.35-1.38 (m, 1H), 3.44 (q, *J* = 6.5 Hz, 1H), 3.77 (s, 3H), 4.10 (s, 1H), 6.65 (d, *J* = 10.5 Hz, 1H), 6.99 (q, *J* = 3.0 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 1H); **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = 11.6, 15.8, 17.7, 29.7, 31.4, 53.4, 55.7, 107.9, 117.8, 119.0, 124.9, 145.5, 152.1, 194.4; **IR** (KBr): 3742, 3442, 3338, 2926, 1641, 1513, 1416, 1160, 821, 628, 512, 421. **ESI-MS** *m/z* ($[M + H]^+$) 218.3.



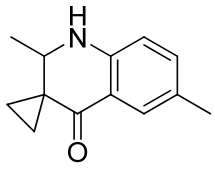
2'-methyl-1'*H*-spiro[cyclopropane-1,3'-quinolin]-4'(2'*H*)-one

(**3c**) Pale yellow solid, m.p.94-97 °C; **^{1}H-NMR** (500 MHz, $CDCl_3$): δ = 0.84-0.92 (m, 2H), 1.21 (d, *J* = 6.5 Hz, 3H), 1.23-1.27 (m, 1H), 1.39-1.43 (m, 1H), 3.43 (q, *J* = 6.5 Hz, 1H), 4.35 (s, 1H), 6.67 (d, *J* = 8.0 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.28-7.32 (m, 1H), 7.38 (q, *J* = 3.0 Hz, 1H); **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = 114.4, 16.2, 17.9, 31.4, 53.3, 116.1, 117.8, 118.9, 127.4, 135.0, 150.5, 194.5; **IR** (KBr): 3745, 3429, 3345, 2924, 1645, 1513, 751, 623, 525, 421. **HRMS** Calcd for $C_{12}H_{14}NO$ ($[M + H]^+$) 188.1075; Found 188.1079.



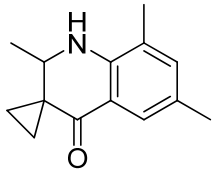
2',8'-dimethyl-1'*H*-spiro[cyclopropane-1,3'-quinolin]-4'(2'*H*)-one

(**3d**) Pale yellow solid, m.p.79-81 °C; **^{1}H-NMR** (500 MHz, $CDCl_3$): δ = 0.85-0.93 (m, 2H, 1.23 (d, *J* = 7.0 Hz, 3H), 1.25-1.27 (m, 1H), 1.38-1.42 (m, 1H), 2.18 (s, 3H), 3.49 (q, *J* = 6.5 Hz, 1H), 4.20 (s, 1H), 6.68 (t, *J* = 8.0 Hz, 1H), 7.22 (t, *J* = 7.0 Hz, 1H), 7.76 (d, *J* = 7.5 Hz, 1H); **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = 11.3, 16.0, 16.9, 18.2, 31.1, 53.1, 117.1, 118.6, 122.8, 125.4, 135.6, 148.7, 194.7; **IR** (KBr): 3743, 3365, 3063, 2966, 2924, 1646, 1603, 1507, 1459, 1377, 1228, 745, 588, 413. **ESI-MS** *m/z* ($[M + H]^+$) 202.2.



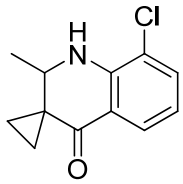
2',6'-dimethyl-1'*H*-spiro[cyclopropane-1,3'-quinolin]-4'(2'*H*)-one

(**3e**) Pale yellow solid, m.p.69-71 °C; **^{1}H-NMR** (500 MHz, $CDCl_3$): δ = 0.83-0.91(m, 2H), 1.20 (d, *J* = 7.0 Hz, 3H), 1.23-1.26 (m, 1H), 1.37-1.40 (m, 1H), 2.24 (s, 3H), 3.42 (q, *J* = 6.5 Hz, 1H), 4.19 (s, 1H), 6.61 (d, *J* = 8.5 Hz, 1H), 7.14 (q, *J* = 2.0 Hz, 1H), 7.64 (s, 1H); **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = 11.5, 16.0, 17.8, 20.3, 31.5, 53.4, 116.1, 118.8, 126.9, 127.1, 136.2, 148.5, 194.6; **IR** (KBr): 3743, 3441, 3336, 2922, 2855, 1643, 1620, 1510, 1316, 1162, 819, 667, 630, 531. **ESI-MS** *m/z* ($[M + H]^+$) 202.2.



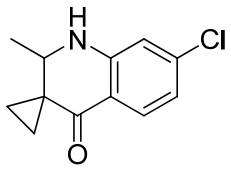
2',6',8'-trimethyl-1'*H*-spiro[cyclopropane-1,3'-quinolin]-4'(2'*H*)-one

(**3f**) Pale yellow solid, m.p.74-76 °C; **^{1}H-NMR** (500 MHz, $CDCl_3$): δ = 0.84-0.92 (m, 2H), 1.21 (d, *J* = 6.5 Hz, 3H), 1.23-1.26 (m, 1H) , 1.36-1.40 (m, 1H), 2.22 (s, 3H), 2.23 (s, 3H), 3.47 (q, *J* = 6.5 Hz, 1H), 4.09 (s, 1H), 7.06 (s, 1H), 7.56 (s, 1H); **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = 11.3, 15.9 , 16.8, 18.1, 20.2, 31.2, 53.1, 118.5, 122.9, 124.8, 126.3, 137.0, 146.7, 194.8; **IR** (KBr): 3744, 3375, 2971, 2926, 1644, 1512, 1317, 1229, 870, 770, 514, 427; **HRMS** Calcd for $C_{14}H_{18}NO$ ($[M + H]^+$) 216.1388; Found 216.1405.



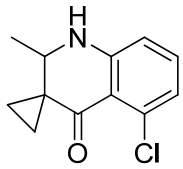
8'-chloro-2'-methyl-1'*H*-spiro[cyclopropane-1,3'-quinolin]-4'(2'*H*)-one

(**3g**) Pale yellow solid, m.p.122-124 °C; **^{1}H-NMR** (500 MHz, $CDCl_3$): δ = 0.87-0.90 (m, 1H), 0.91-0.96 (m, 1H), 1.25 (d, *J* = 6.5 Hz, 3H), 1.22-1.28 (m, 1H), 1.43-1.47 (m, 1H), 3.50 (q, *J* = 2.0 Hz, 1H), 4.91 (s, 1H), 6.68 (t, *J* = 8.0 Hz, 1H), 7.41 (q, *J* = 3.0 Hz, 1H), 7.78 (q, *J* = 3.0 Hz, 1H); **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = 11.5, 16.8, 18.1, 31.1, 53.1, 117.2, 119.9 , 120.0, 126.2, 134.3, 146.3, 193.7; **IR** (KBr): 3392, 3350, 2968, 2926, 1655, 1600, 1501, 1372, 1307, 1228, 1131, 1067, 741, 619, 579. **ESI-MS** *m/z* ($[M + H]^+$) 222.1.



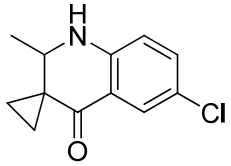
7'-chloro-2'-methyl-1'*H*-spiro[cyclopropane-1,3'-quinolin]-4'(2'*H*)-one

(**3h**) Yellow solid, m.p.111-113 °C; **^{1}H-NMR** (500 MHz, $CDCl_3$): δ = 0.76-0.85 (m, 2H), 1.13 (d, *J* = 7.0 Hz, 3H), 1.15-1.27 (m, 1H), 1.32-1.38 (m, 1H), 3.31-3.35 (m, 1H), 4.42 (s, 1H), 6.60 (d, *J* = 7.0 Hz, 1H), 6.61 (s, 1H), 7.68 (d, *J* = 9.0 Hz, 1H); **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = 11.5, 16.8, 18.1, 31.3, 53.5, 115.4, 117.3, 118.3, 129.0, 141.0, 150.9, 193.6; **IR** (KBr): 3745, 3441, 3338, 2975, 1645, 1608, 1512, 1349, 1246, 1078, 987, 861, 750, 525, 419. **ESI-MS** *m/z* ($[M + H]^+$) 222.1.



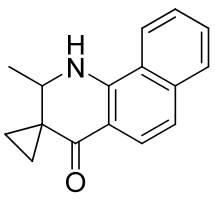
5'-chloro-2'-methyl-1'*H*-spiro[cyclopropane-1,3'-quinolin]-4'(2'*H*)-one

(**3h′**) Yellow oil; **^{1}H-NMR** (500 MHz, $CDCl_3$): δ = 0.89 (d, *J* = 3.0 Hz, 2H), 1.22 (d, *J* = 6.5 Hz, 3H), 1.23-1.31 (m, 1H), 1.41-1.44 (m, 1H), 3.43 (d, *J* = 6.5 Hz, 1H), 3.65 (s, 1H), 6.62 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.14 (t, *J* = 7.5 Hz, 1H); **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = 12.2, 16.9, 17.6, 32.3, 52.4, 115.3, 115.6, 121.1, 133.9, 135.0, 152.9, 192.6; **IR** (KBr): 3745, 3430, 3343, 2967, 2923, 1641, 1609, 1480, 1452, 1371, 1227, 989, 752, 711, 624, 526. **ESI-MS** *m/z* ($[M + H]^+$) 222.05.



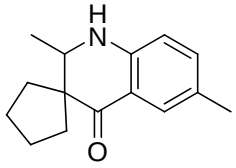
6'-chloro-2'-methyl-1'*H*-spiro[cyclopropane-1,3'-quinolin]-4'(2'*H*)-one

(**3i**) Pale yellow solid, m.p.117-121 °C; **^{1}H-NMR** (500 MHz, $CDCl_3$): δ = 0.86-0.94 (m, 2H), 1.21 (d, *J* = 6.5 Hz, 3H), 1.24-1.27 (m, 1H), 1.40-1.44 (m, 1H), 3.43 (q, *J* = 2.0 Hz, 1H), 4.34 (s, 1H), 6.63 (d, *J* = 8.5 Hz, 1H), 7.24 (q, *J* = 2.5 Hz, 1H), 7.79 (d, *J* = 2.0 Hz, 1H); **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = 11.6, 16.6, 17.9, 31.3, 53.3, 117.6, 119.6, 123.1, 126.7, 134.8, 148.8, 193.4; **IR** (KBr): 3744, 3347, 3064, 2964, 2924, 1640, 1615, 1507, 1411, 1175, 813, 622, 533, 424. **HRMS** Calcd for $C_{12}H_{13}ClNO$ ($[M + H]^+$) 222.0686; Found 222.0679.



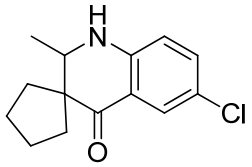
2-methyl-1*H*-spiro[benzo[*h*]quinoline-3,1'-cyclopropan]-4(2*H*)-one

(**3j**) Yellow solid, m.p.125-128 °C; **^{1}H-NMR** (500 MHz, $CDCl_3$): δ = 0.77-0.85 (m, 2H), 1.16-1.19 (m, 1H), 1.21 (d, *J* = 6.5 Hz, 3H), 1.36-1.40 (m, 1H), 3.50 (d, *J* = 6.5 Hz, 1H), 5.38 (s, 1H), 7.03 (d, *J* = 8.5 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 8.5 Hz, 1H); **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = 11.0, 16.0, 17.7, 30.5, 53.4, 113.2, 117.3, 121.0, 123.0, 123.3, 125.6, 128.8, 128.9, 137.0, 148.0, 193.9; **IR** (KBr): 3745, 3357, 2961, 2924, 2856, 1626, 1539, 1425, 1387, 1224, 1118, 788, 760, 573, 454. **ESI-MS** *m/z* ($[M + H]^+$) 238.2.



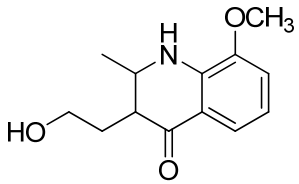
2',6'-dimethyl-1'*H*-spiro[cyclopentane-1,3'-quinolin]-4'(2'*H*)-one

(**3l**) Yellow solid, m.p.106-108 °C; **^{1}H-NMR** (500 MHz, $CDCl_3$): δ = 1.20 (d, *J* = 6.5 Hz, 3H), 1.59-1.71 (m, 6H), 1.85 (d, *J* = 8.0 Hz, 1H), 2.10 (t, *J* = 6.5 Hz, 1H), 2.23 (s, 3H), 3.48 (q, *J* = 6.5 Hz, 1H), 4.23 (s, 1H), 6.53 (d, *J* = 8.5 Hz, 1H), 7.10 (d, *J* = 8.5 Hz, 1H), 7.63 (s, 1H); **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = 16.23 20.2, 26.2, 26.4, 29.6, 33.0, 56.4, 56.8, 115.3, 117.1, 126.6, 127.7, 135.9, 147.5, 198.5; **IR** (KBr): 3338, 2936, 2862, 1650, 1513, 1297, 1145, 984, 813. **ESI-MS** *m/z* ($[M + H]^+$) 230.3.



6'-chloro-2'-methyl-1'*H*-spiro[cyclopentane-1,3'-quinolin]-4'(2'*H*)-one

(**3m**) Yellow solid, m.p.139-143 °C; **^{1}H-NMR** (500 MHz, $CDCl_3$): δ = 1.20 (d, *J* = 6.5 Hz, 3H), 1.58-1.62 (m, 2H), 1.65-1.71 (m, 4H), 1.86 (d, *J* = 5.0 Hz, 1H), 2.06 (t, *J* = 6.0 Hz, 1H), 3.50 (q, *J* = 6.5 Hz, 1H), 4.36 (s, 1H), 6.55 (d, *J* = 8.5 Hz, 1H), 7.20 (q, *J* = 6.5 Hz, 1H), 7.78 (d, *J* = 2.5 Hz, 1H); **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = 16.2, 26.1, 26.4, 29.6, 33.1, 56.3, 56.6, 116.8, 117.9, 122.6, 127.4, 134.5, 147.8, 197.2; **IR** (KBr): 3365, 3186, 2951, 1653, 1568, 1454, 1387, 980, 922, 793, 525. **ESI-MS** *m/z* ($[M + H]^+$) 250.1.



3-(2-hydroxyethyl)-8-methoxy-2-methyl-2,3-dihydroquinolin-4(1*H*)-one

(**4a**) Yellow solid, m.p.120-123 °C; **^{1}H-NMR** (500 MHz, $CDCl_3$): δ = 1.33 (d, *J* = 7.0 Hz, 3H), 1.92-196 (m, 2H), 2.50 (q, *J* = 7.5 Hz, 1H), 3.17 (s, 1H), 3.63-3.69 (m, 1H), 3.70-3.74 (m, 2H), 3.86 (s, 3H), 4.93 (s, 1H), 6.63 (t, *J* = 8.0 Hz, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 7.42 (t, *J* = 6.5 Hz, 1H); **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = 20.0, 30.6, 50.1, 52.1, 55.6, 60.6, 113.6, 116.1, 117.3, 118.8, 141.1, 146.7, 196.9; **IR** (KBr): 3744,

3443, 3313, 2939, 1649, 1611, 1516, 1233, 1054, 996, 745, 471; **ESI-MS** *m/z* ([M + H]$^+$) 236.2.

III. Summary of Crystal Data

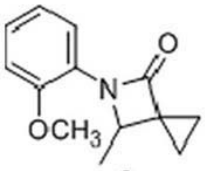
Single-crystal X-ray diffraction data for the reported complex was recorded at a temperature of 293(2) K on a Oxford Diffraction Gemini R Ultra diffractometer, using a ω scan technique with Mo-Kα radiation (λ = 0.71073 Å). The structure was solved by Direct Method of SHELXS-97 and refined by full-matrix least-squares techniques using the SHELXL-97 program.[1] Non-hydrogen atoms were refined with anisotropic temperature parameters, and hydrogen atoms of the ligands were refined as rigid groups. Basic information pertaining to crystal parameters and structure refinement is summarized in Table 1

1 (*a*) G. M. Sheldrick, *SHELXS-97, Program for Solution of Crystal Structures, University of Göttingen,* Germany, 1997; (*b*) G. M. Sheldrick, *SHELXL-97, Program for Refinement of Crystal Structures, University of Göttingen,* Germany, 1997.

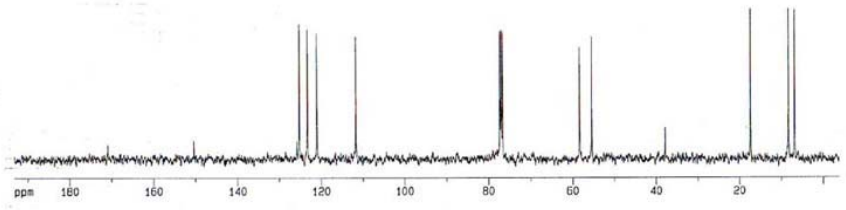
Table 1. Crystal data and structure refinement.

Empirical formula	$C_{13}H_{15}NO_2$
Formula weight	217.26
Temperature	293(2) K
Crystal system	Triclinic,
Space group	P -1
Unit cell dimensions	a = 7.981(3) Å
	b = 8.782(5) Å
	c = 9.476(5) Å
	alpha = 111.031(7) deg.
	beta = 104.521(6) deg.
	gamma = 99.324(6) deg.
Volume	576.3(5) Å^3
Z	2

Calculated density	1.252 Mg/m^3
Absorption coefficient	0.084 mm^{-1}
F(000)	232
Crystal size	0.16 x 0.14 x 0.11 mm
Theta range for data collection	3.79 to 29.19 deg.
Reflections collected / unique	4575 / 2658 [R(int) = 0.0154]
Data / restraints / parameters	2658 / 0 / 145
Goodness-of-fit on F^2	1.030
Final R indices [I>2sigma(I)]	R1 = 0.0481, wR2 = 0.1210
R indices (all data)	R1 = 0.0666, wR2 = 0.1360


O
N
OCH3

2a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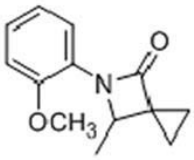
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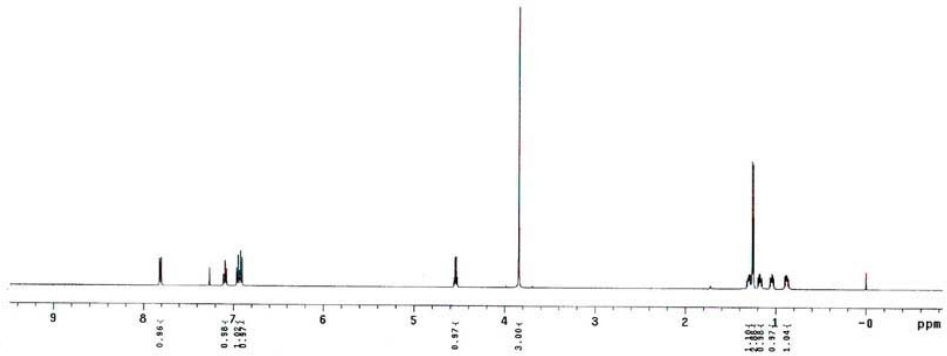
N
OCH3

2a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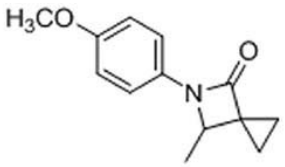
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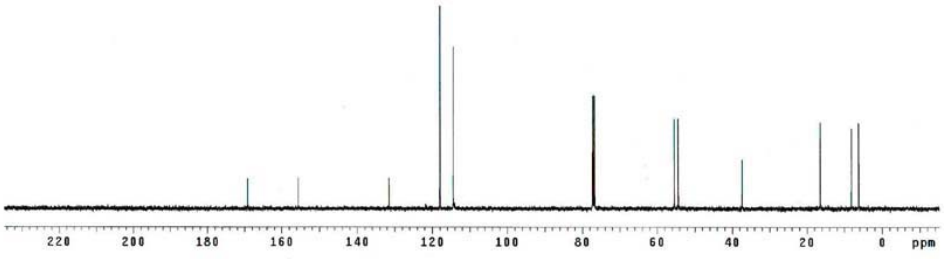
O
N

2b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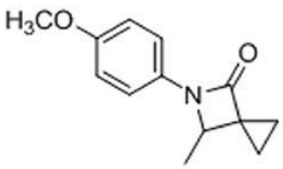
0
ppm


H3CO
O
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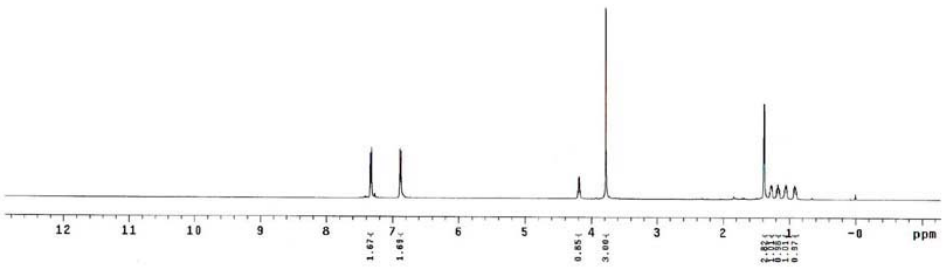
2b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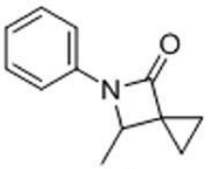

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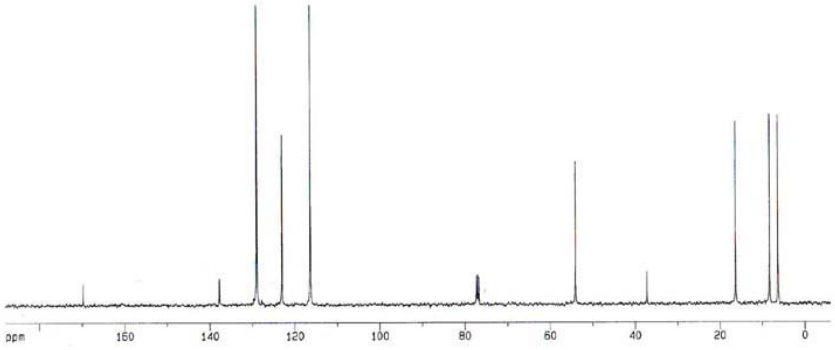

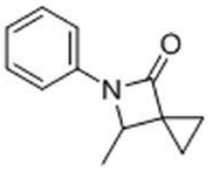

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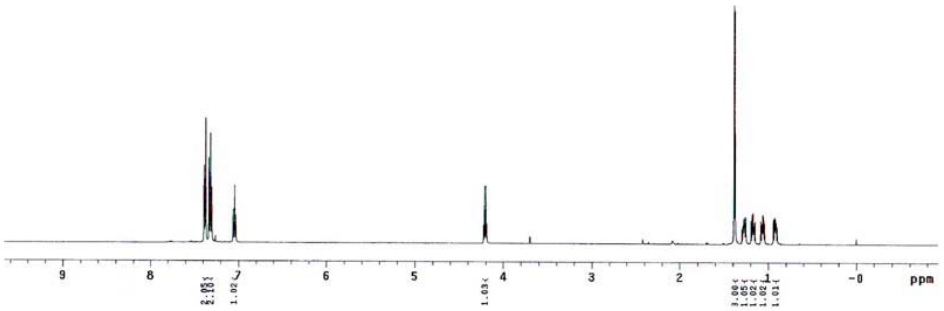

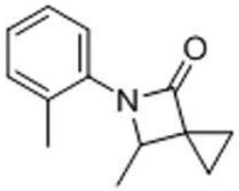
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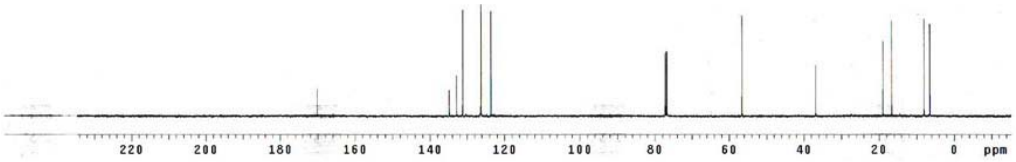
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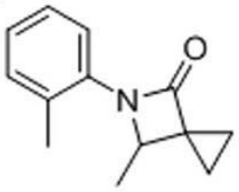
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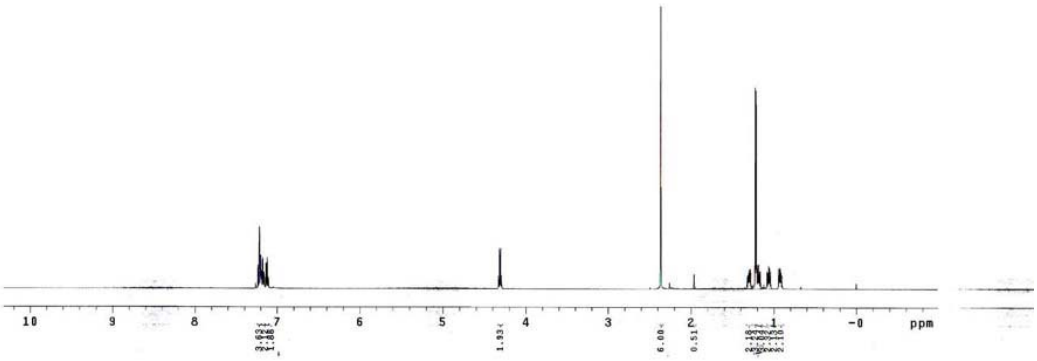
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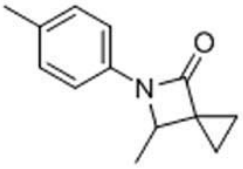

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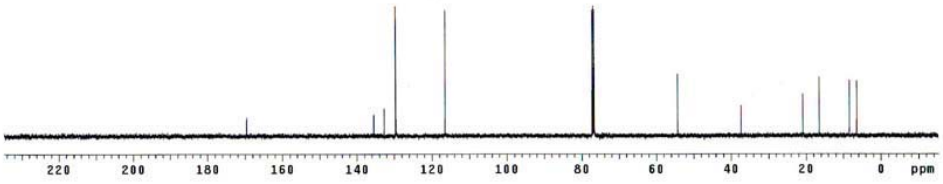

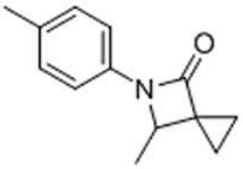

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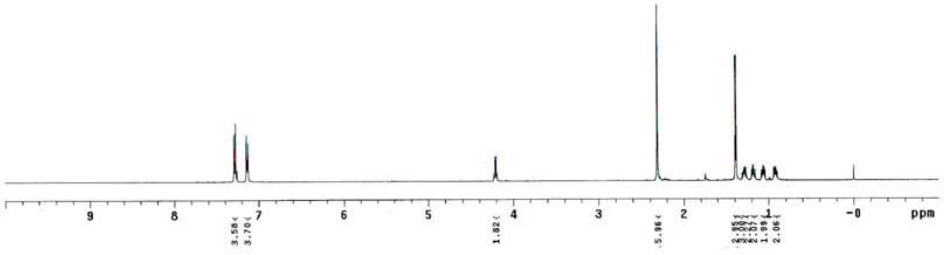

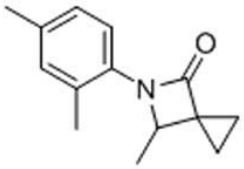

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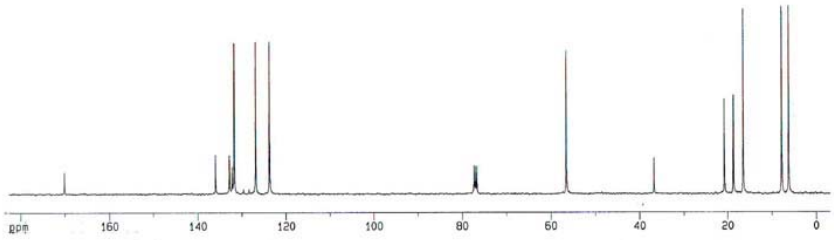

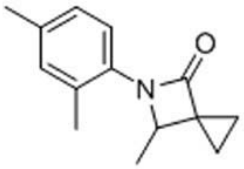

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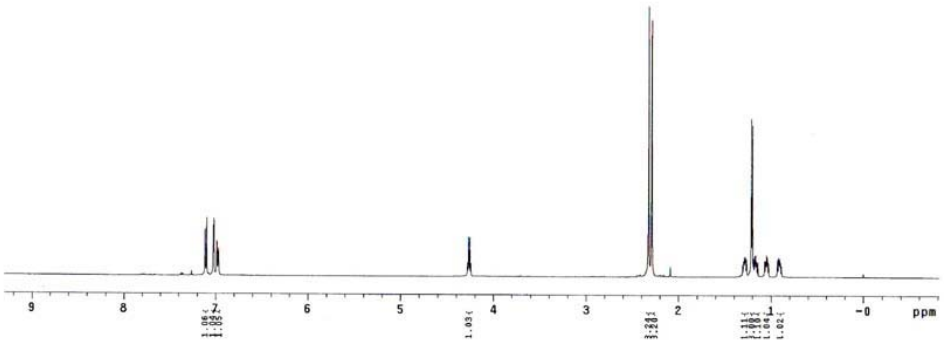

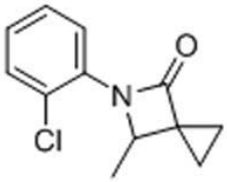
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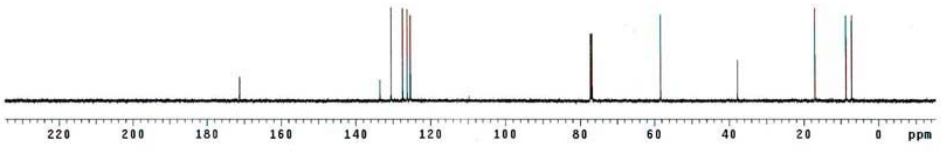
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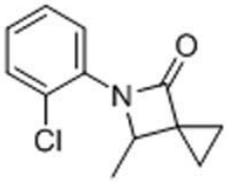
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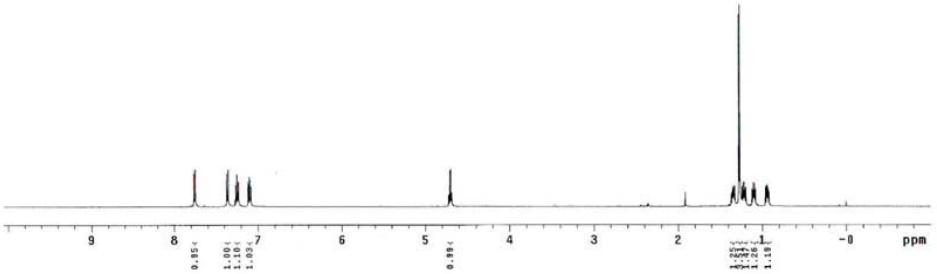
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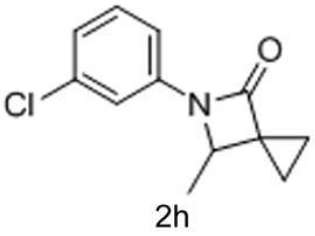
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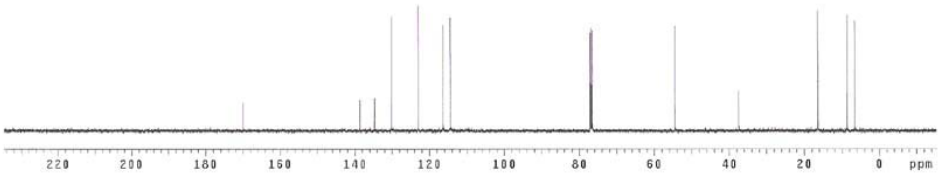
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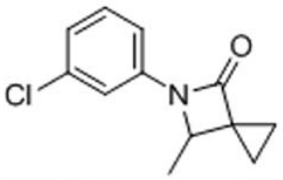
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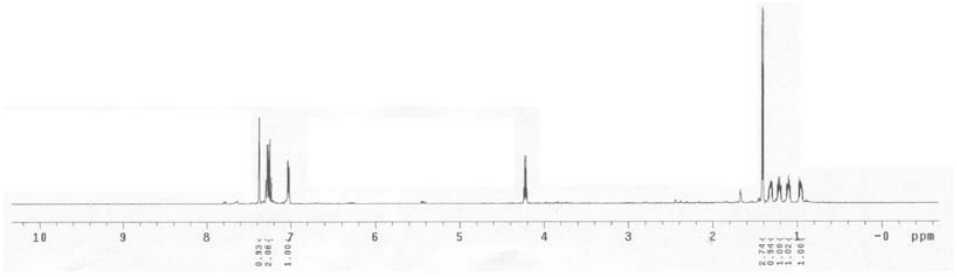
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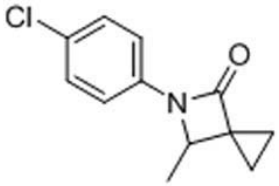
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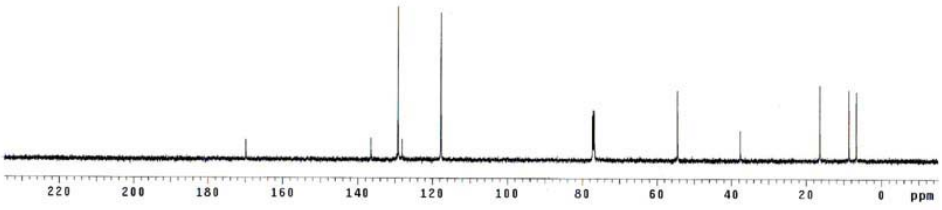
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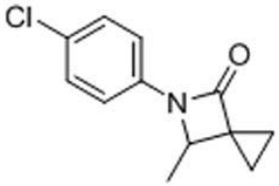
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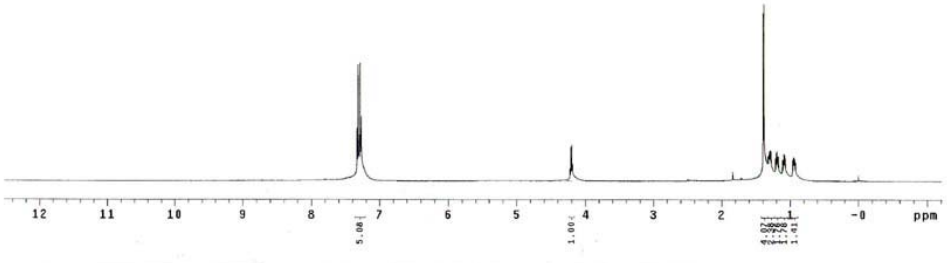
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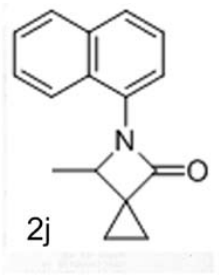
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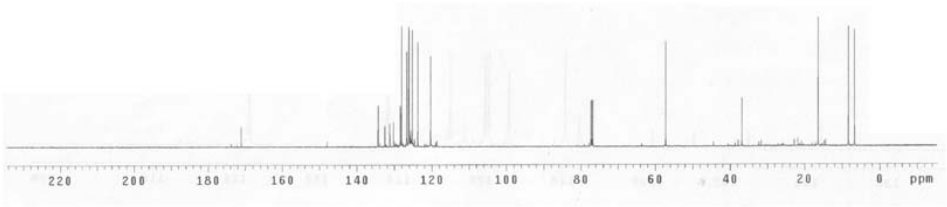
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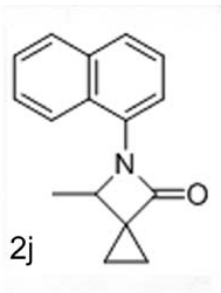
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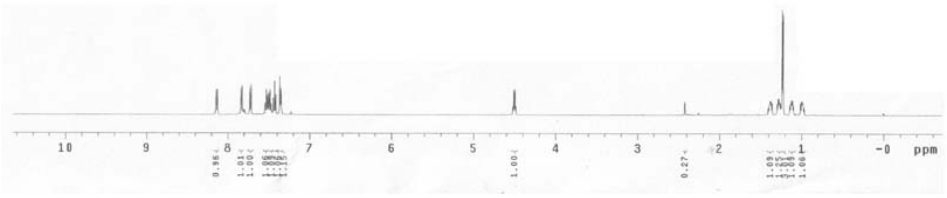
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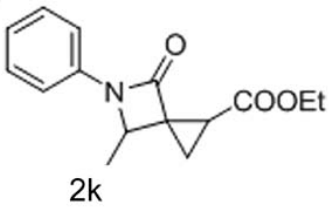
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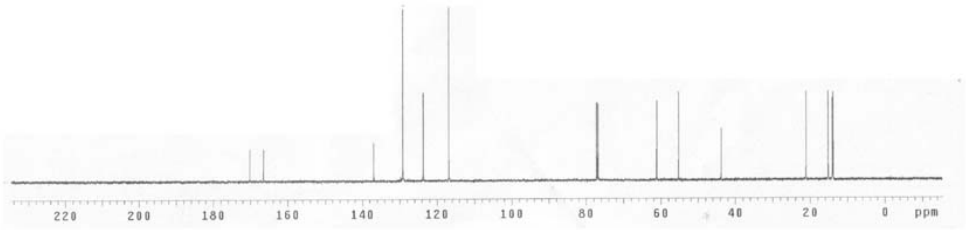
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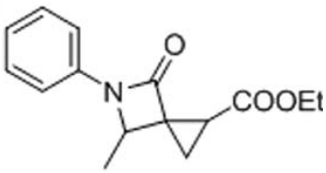
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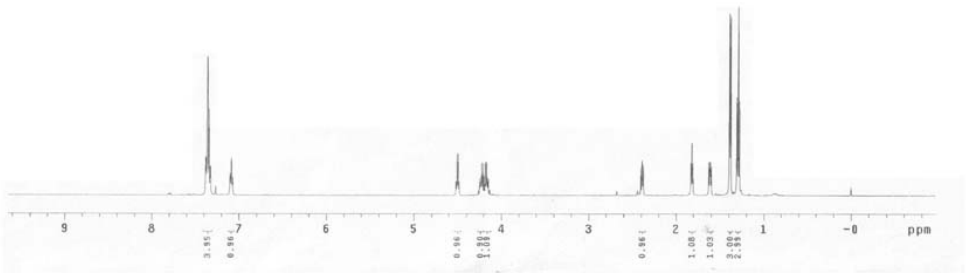
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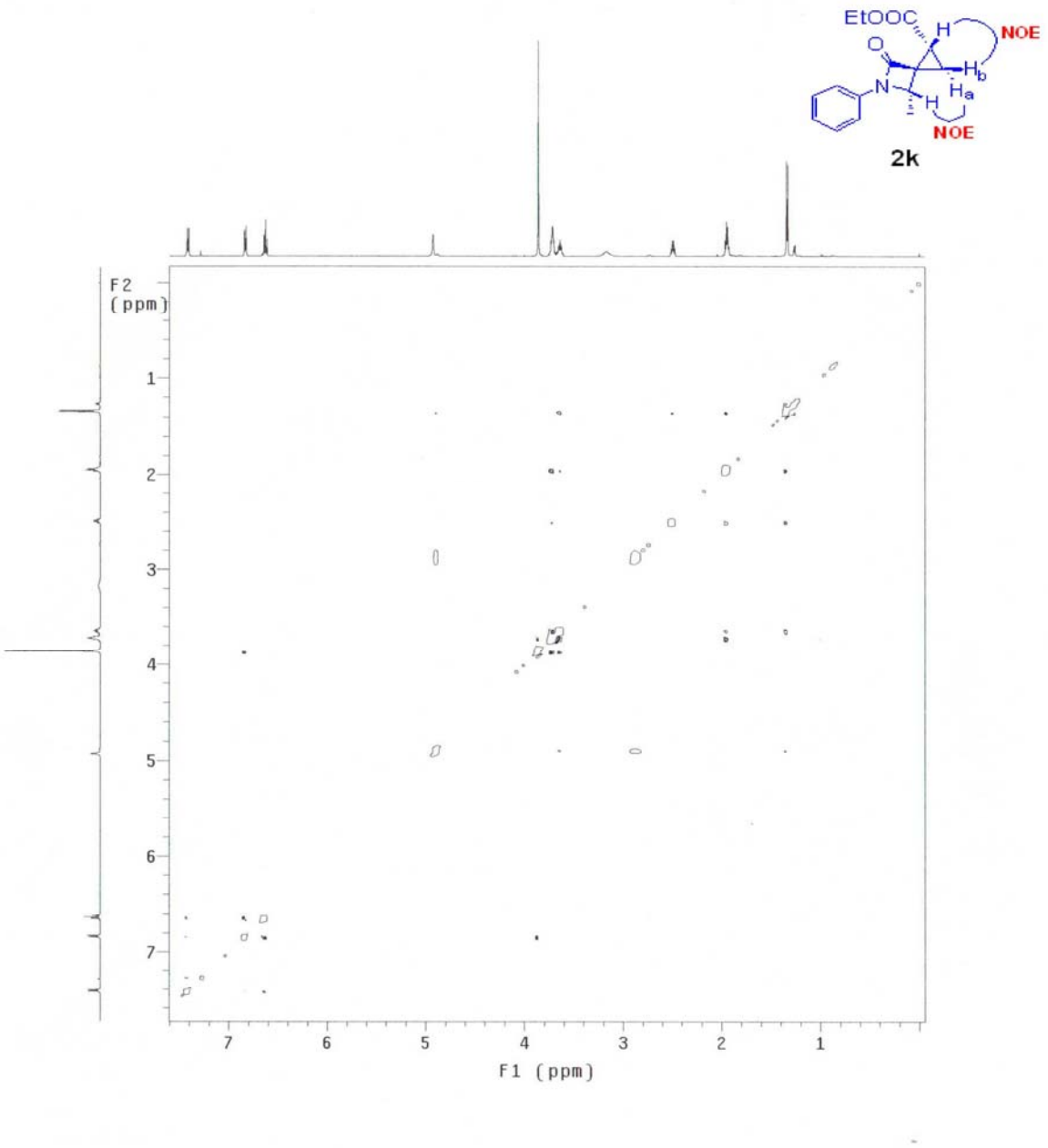

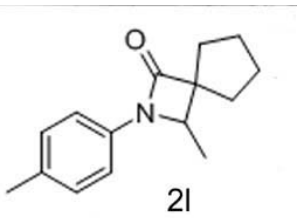
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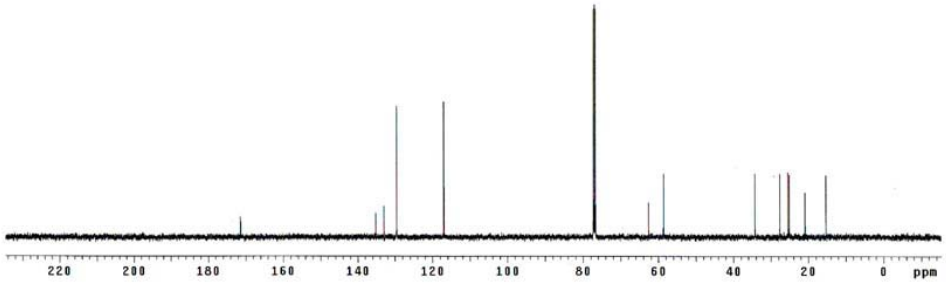
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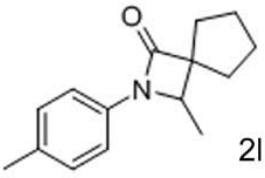
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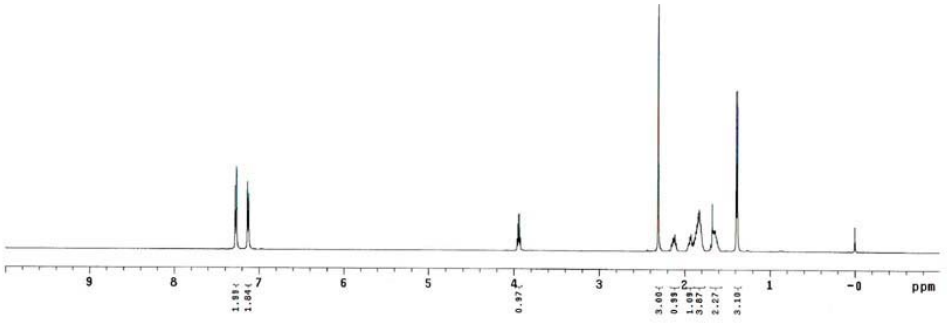
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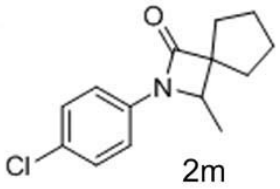
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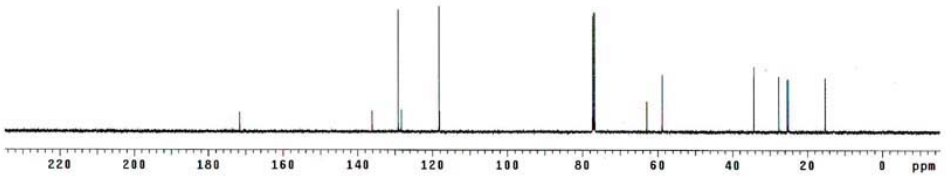
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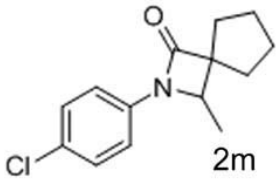
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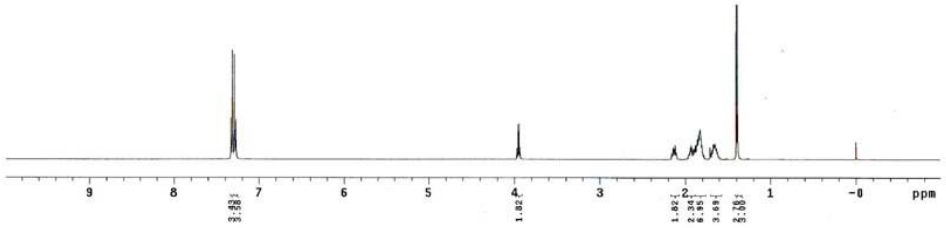
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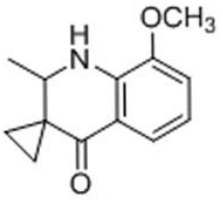
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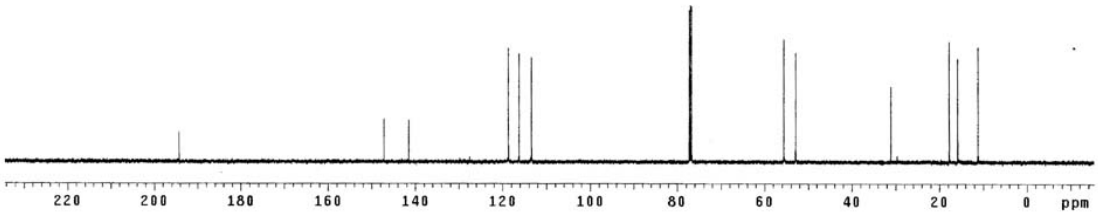
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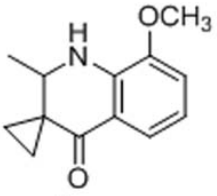
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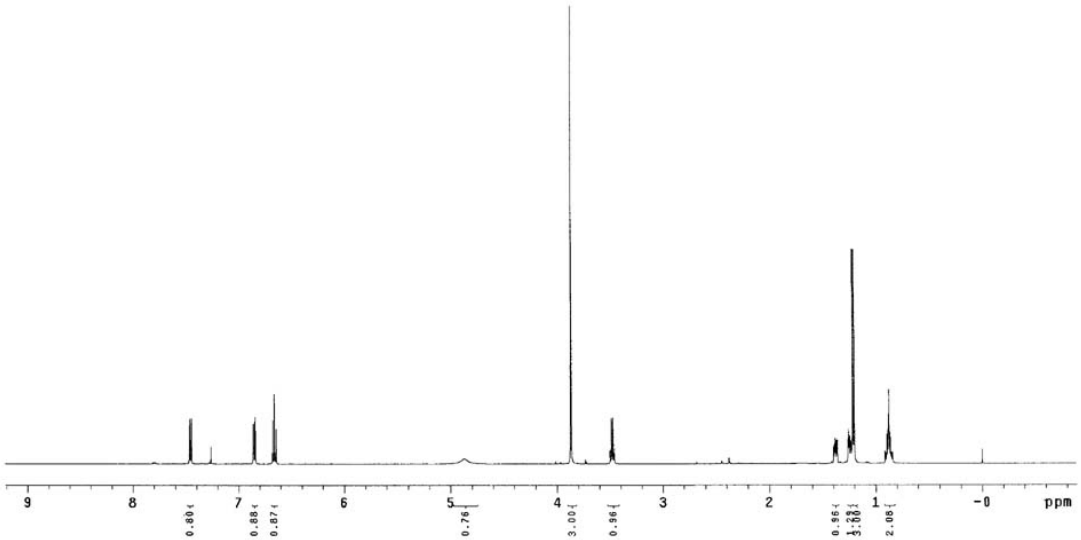
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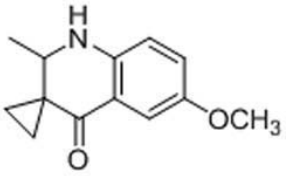
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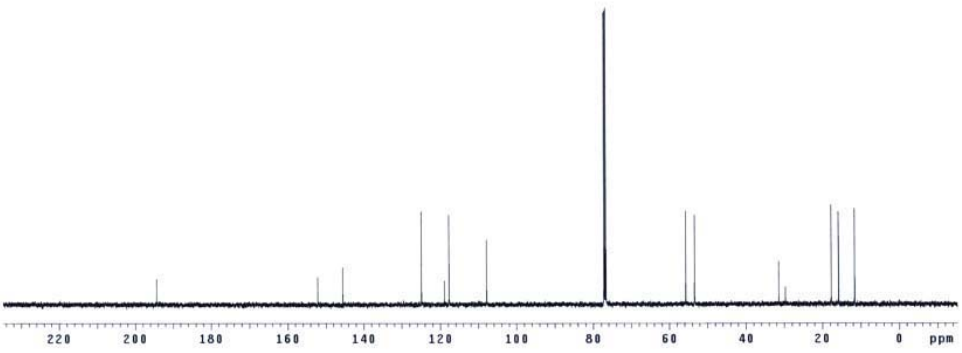
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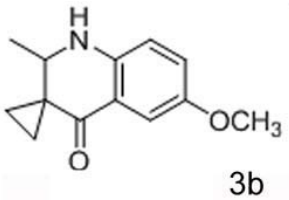
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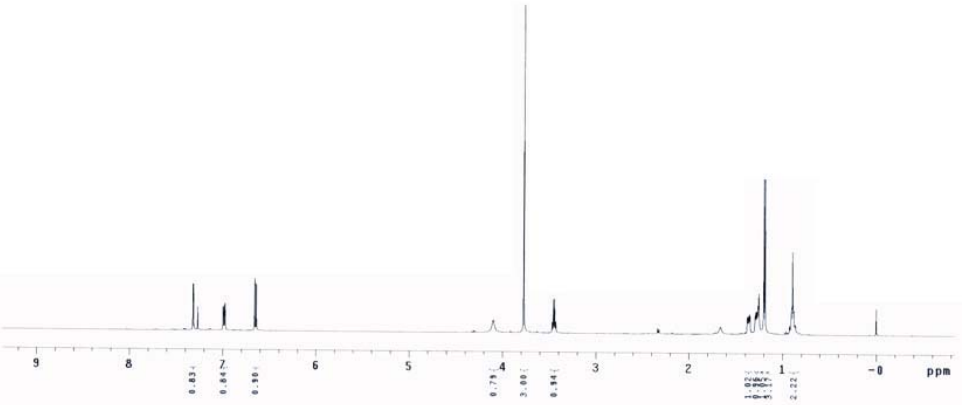
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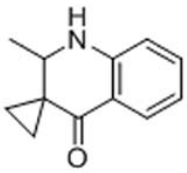

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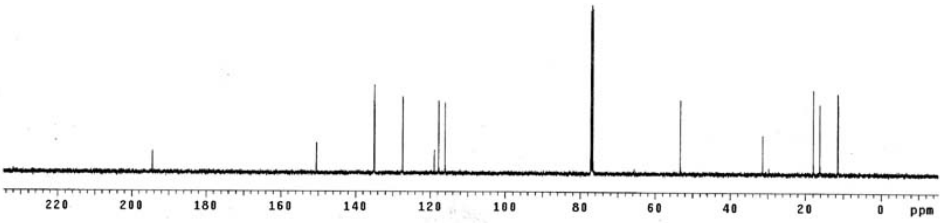

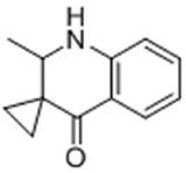

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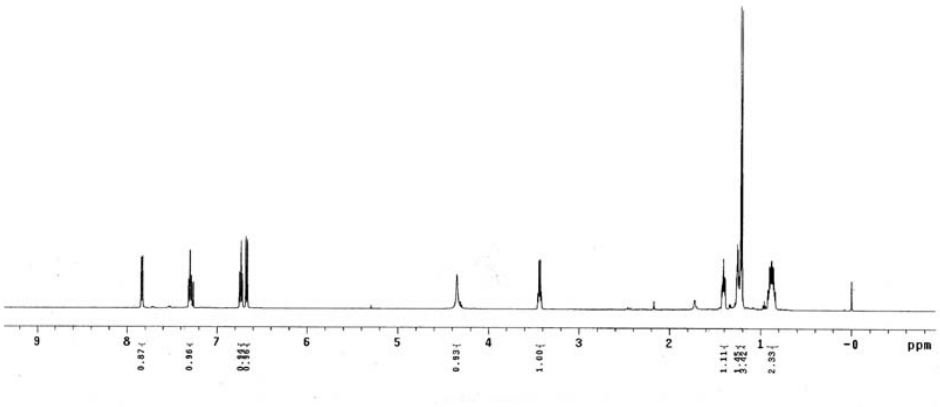

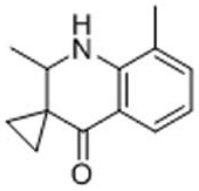
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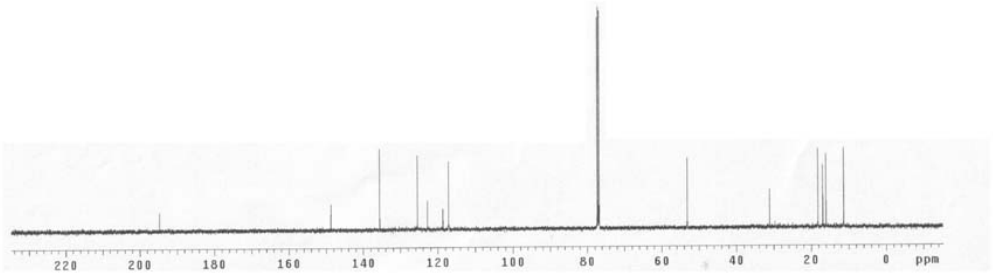
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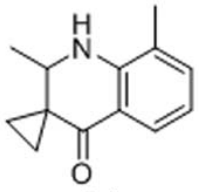
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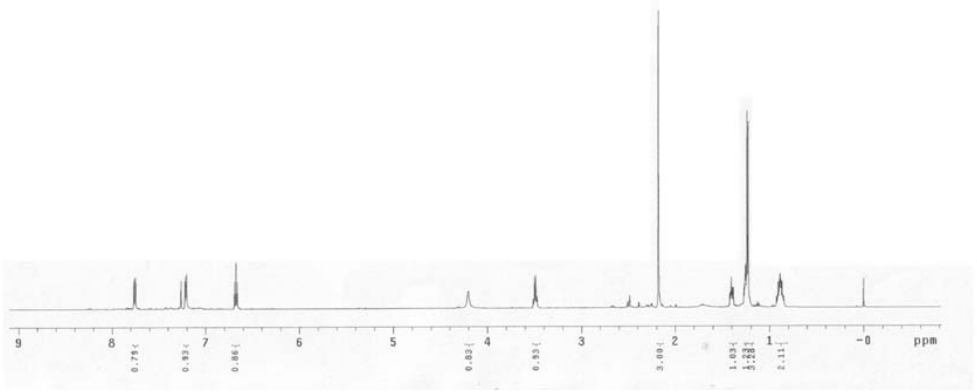
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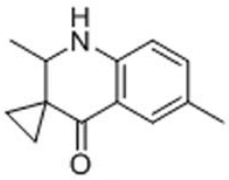
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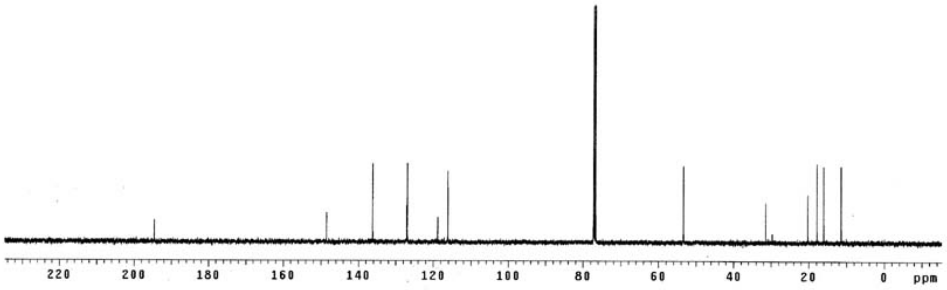
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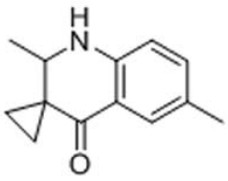
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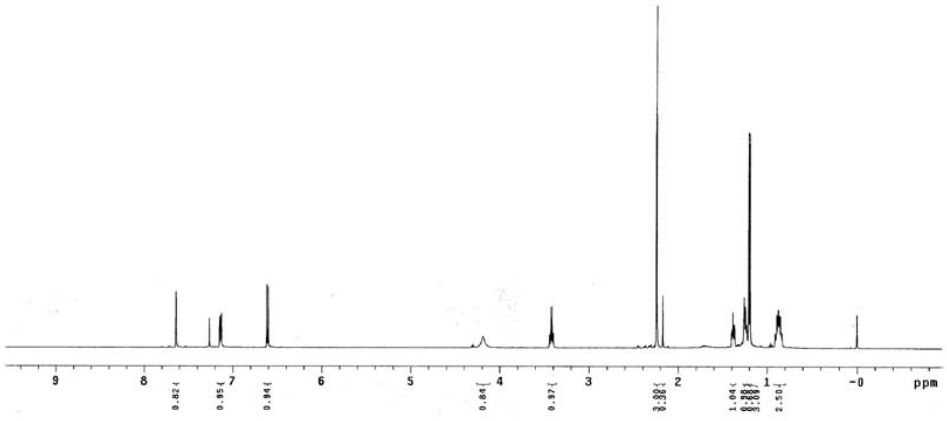
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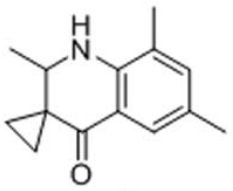
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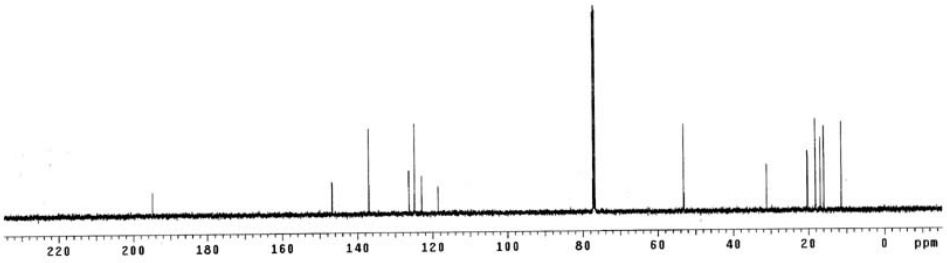
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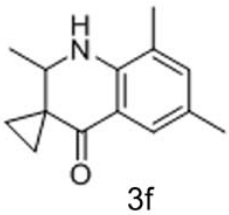
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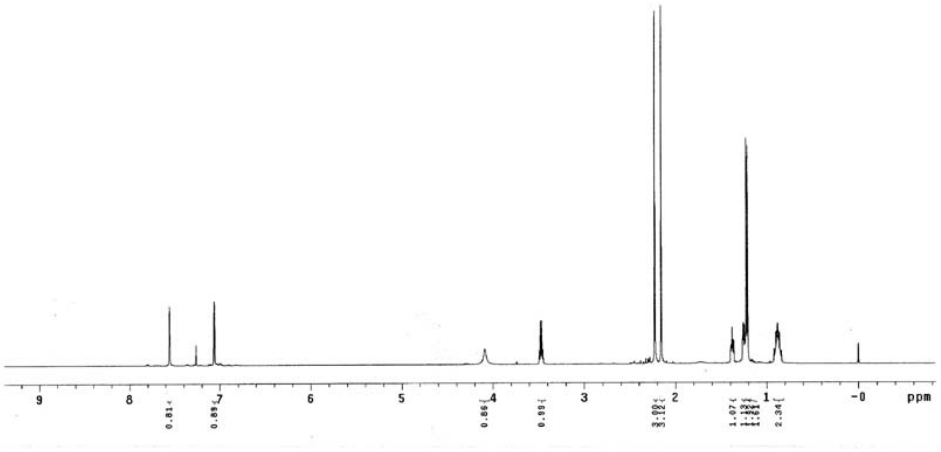
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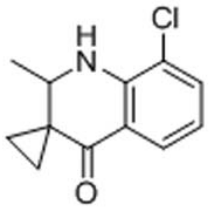
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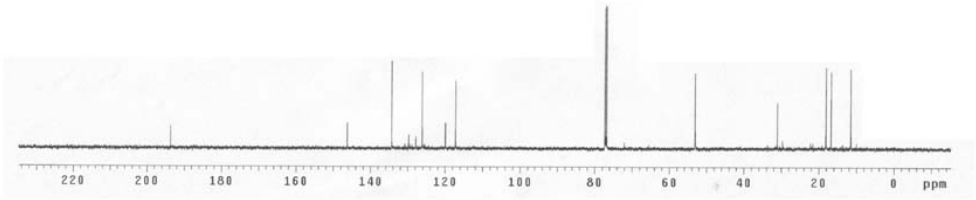
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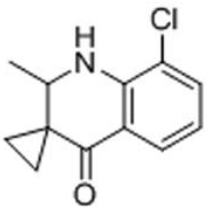
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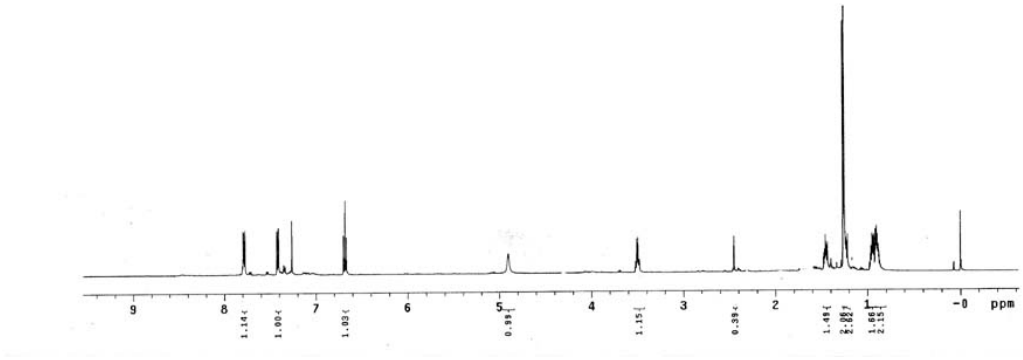
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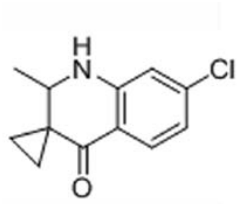
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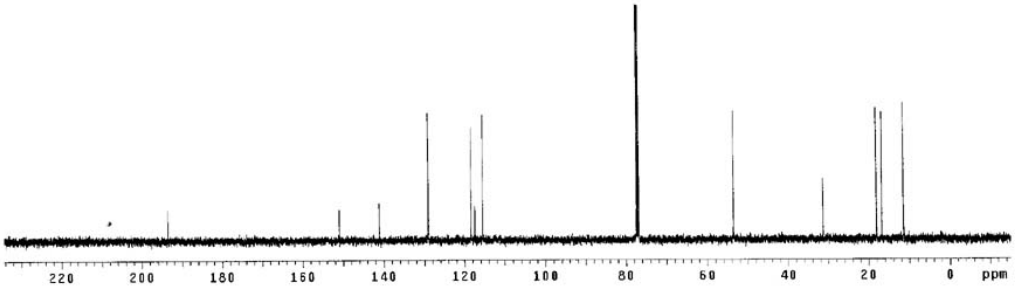
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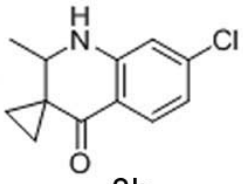
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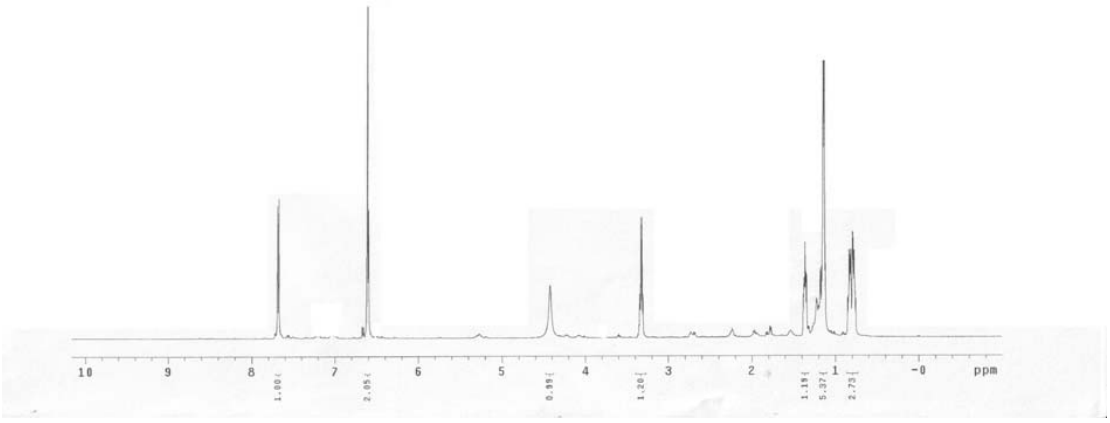
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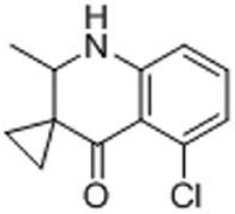
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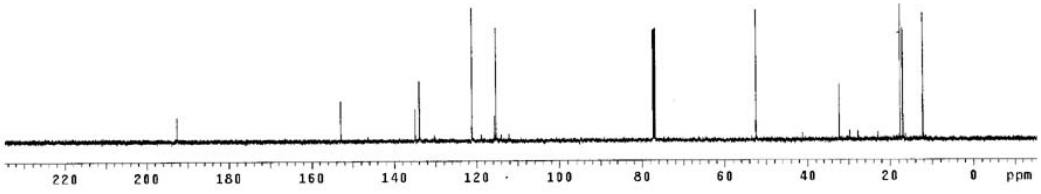
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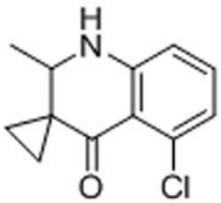
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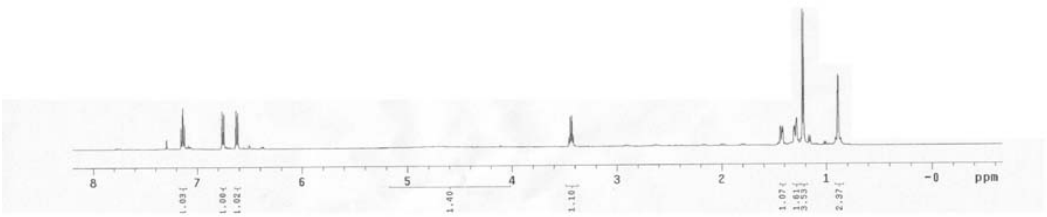
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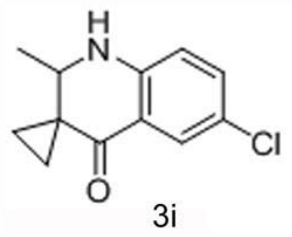
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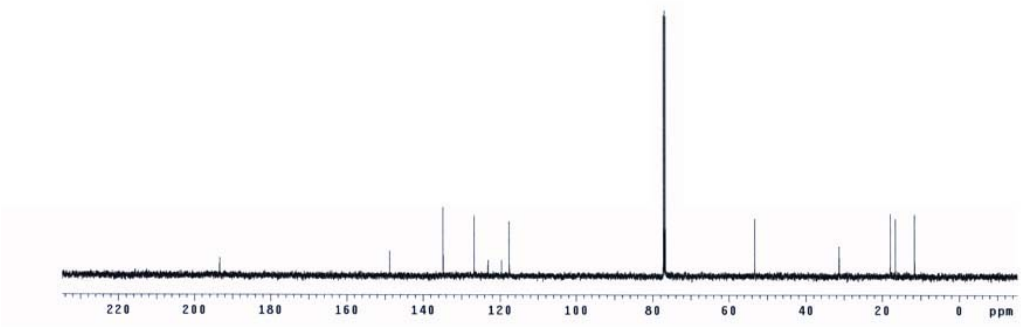
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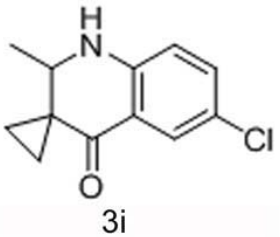
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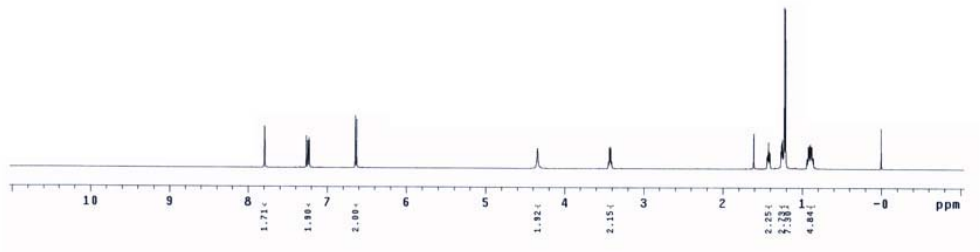
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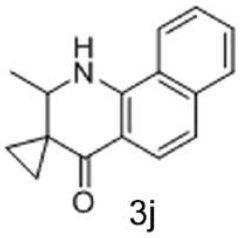
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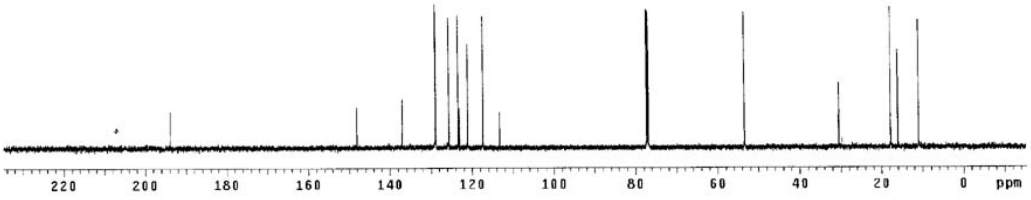
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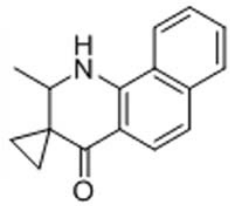
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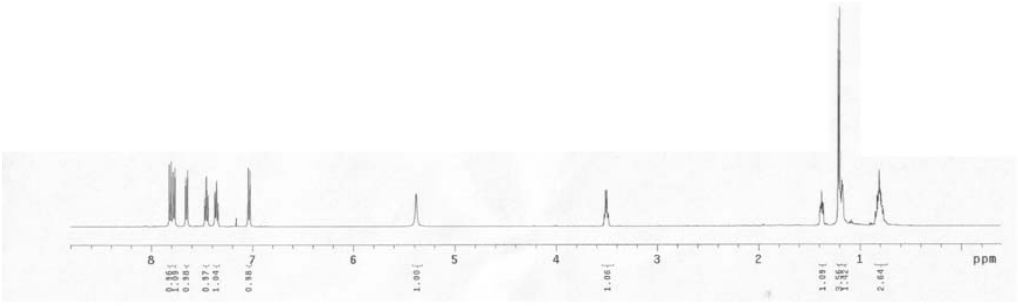
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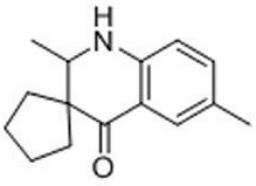

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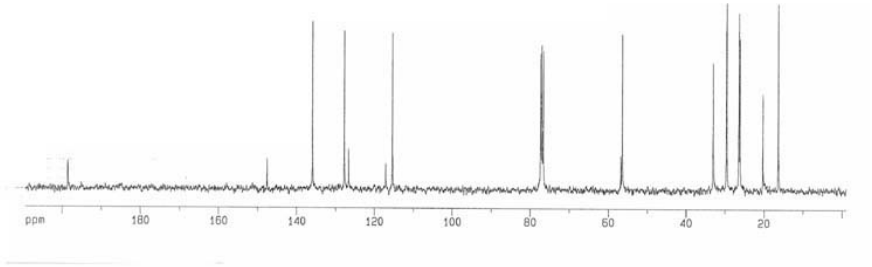

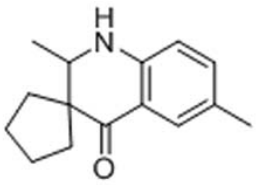

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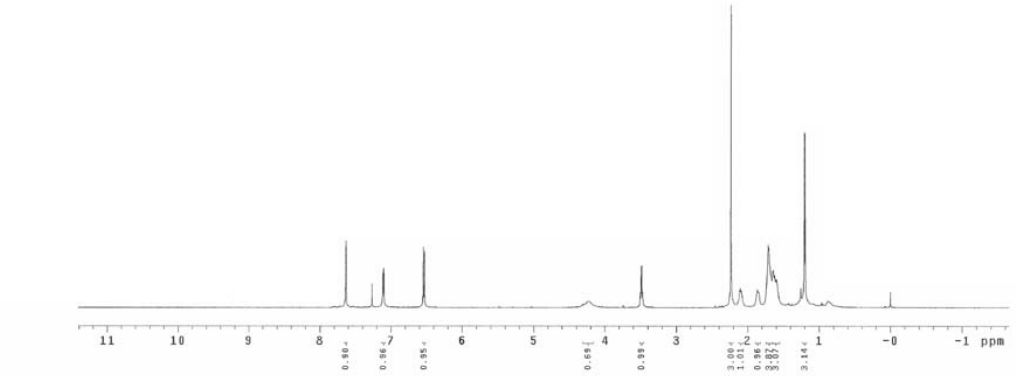

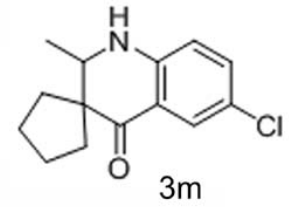

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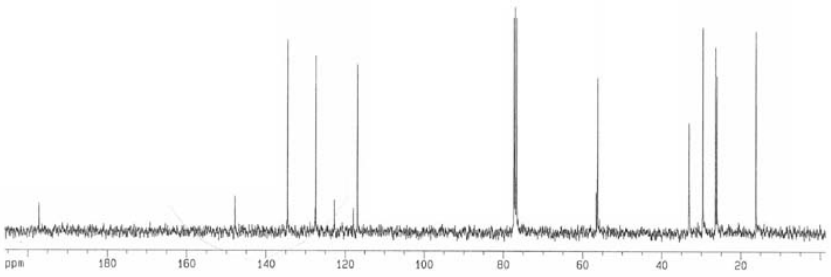

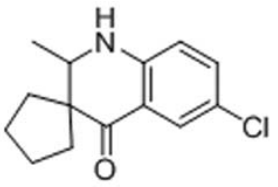

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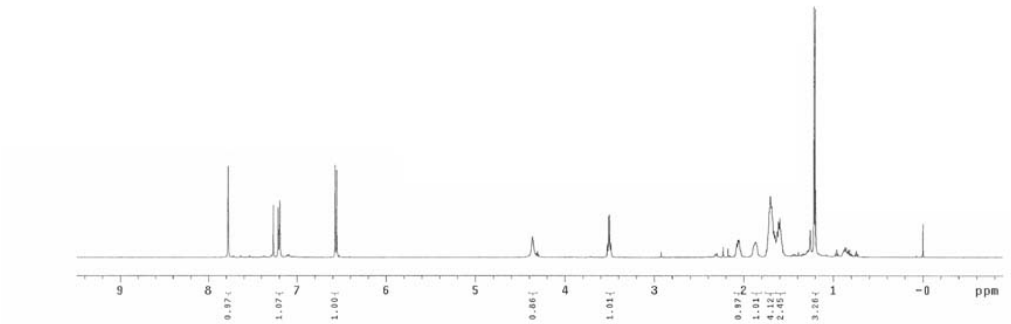

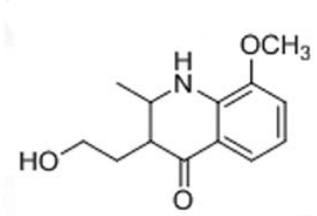
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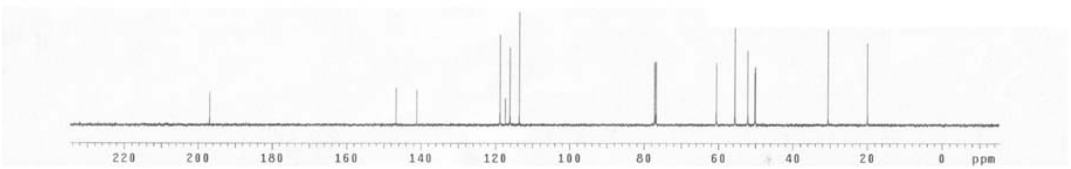
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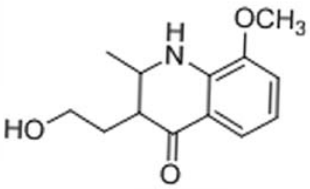
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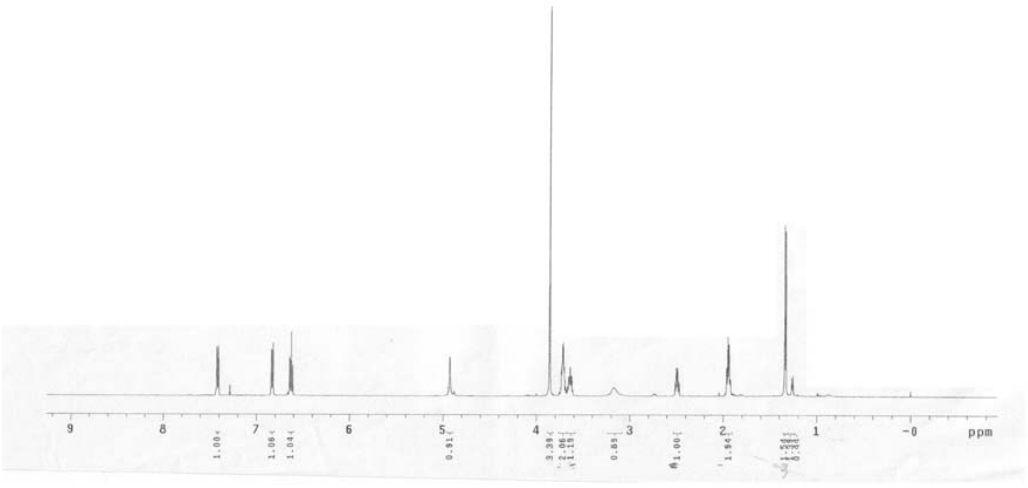
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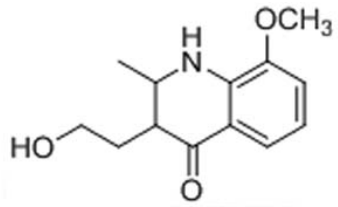

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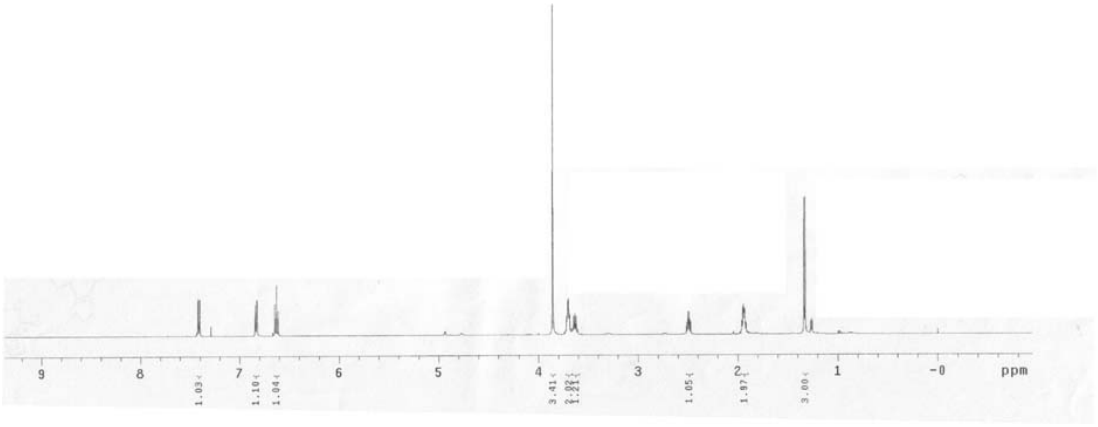

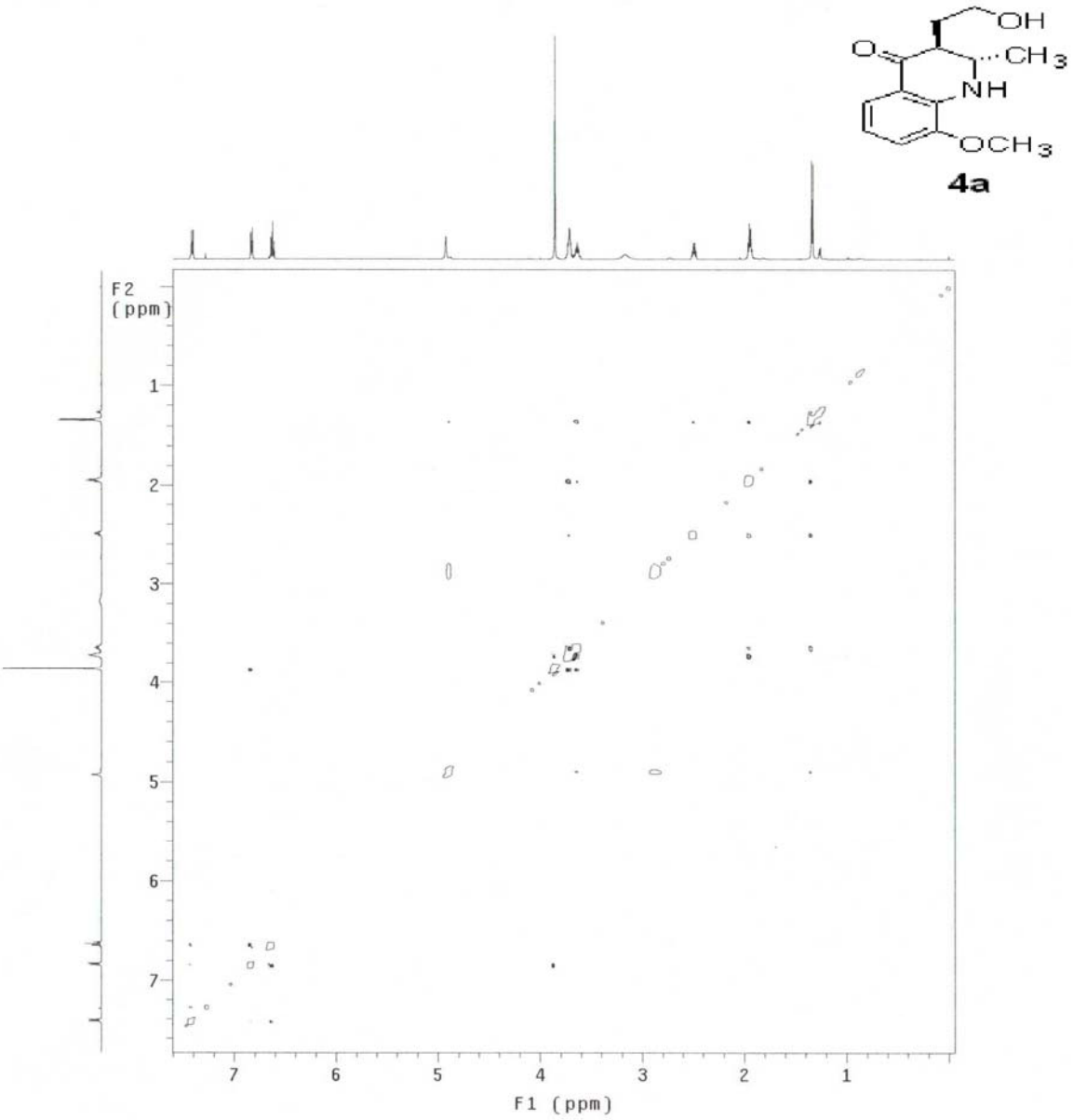
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NH
OCH3
4a
F2
(ppm)
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6
7
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6
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4
3
2
1
F1 (ppm)