Supporting Information

Thermally-induced Intramolecular [2+2] Cycloaddition of acrylamide-tethered alkylidenecyclopropanes

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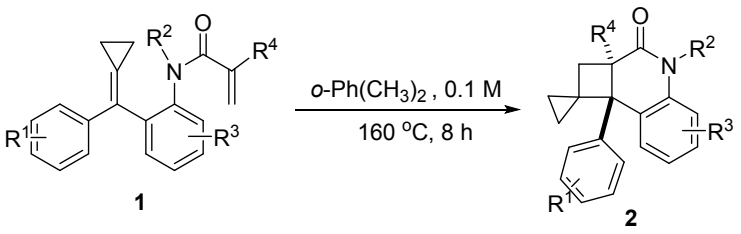
CONTENTS

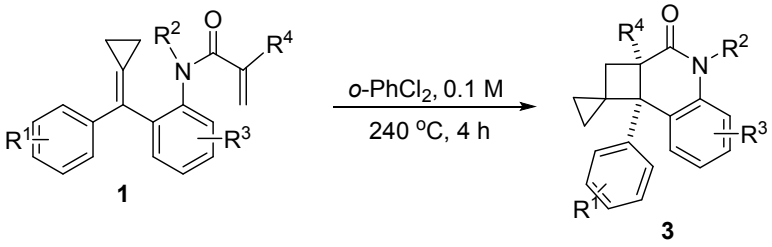
1. General Remarks.

Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. NMR spectra were recorded with a Bruker spectrometer at 400 MHz (^{1}H NMR), 100 MHz (^{13}C NMR) and 376 MHz (^{19}F NMR) in $CDCl_3$, respectively. Chemical shift were reported in ppm down field from internal TMS. Organic solvents used were dried by standard methods when necessary. Commercially available reagents were used without further purification. All reactions were monitored by TLC with Huanghai GF_{254} silica gel coated plates. Flash column chromatography was carried out using 300-400 mesh silica gel at increased pressure. All reactions were performed under argon using standard Schlenk techniques. Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in cm^{-1}. Mass spectra were recorded by ESI and HRMS was measured on a HP-5989 instrument. Substrates **1a-1s** were prepared and characterized according to the procedure in the previous literature.[1]

2. General Procedure for the Synthesis of 2 and 3.

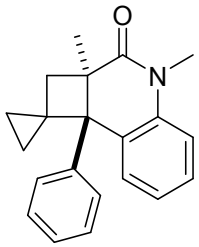


Compound **1** (0.20 mmol) was added to a sealed tube with a magnetic stir bar. *o*-$Ph(CH_3)_2$ (2.0 mL) was added and the reaction tube was heated to 160 °C for 8 h under N_2 atmosphere. The reaction mixture was concentrated in vacuum, and the resulting residue was purified by a silica gel chromatography (eluent: petroleum ether / ethyl acetate = 10:1) to afford the desired product **2**.



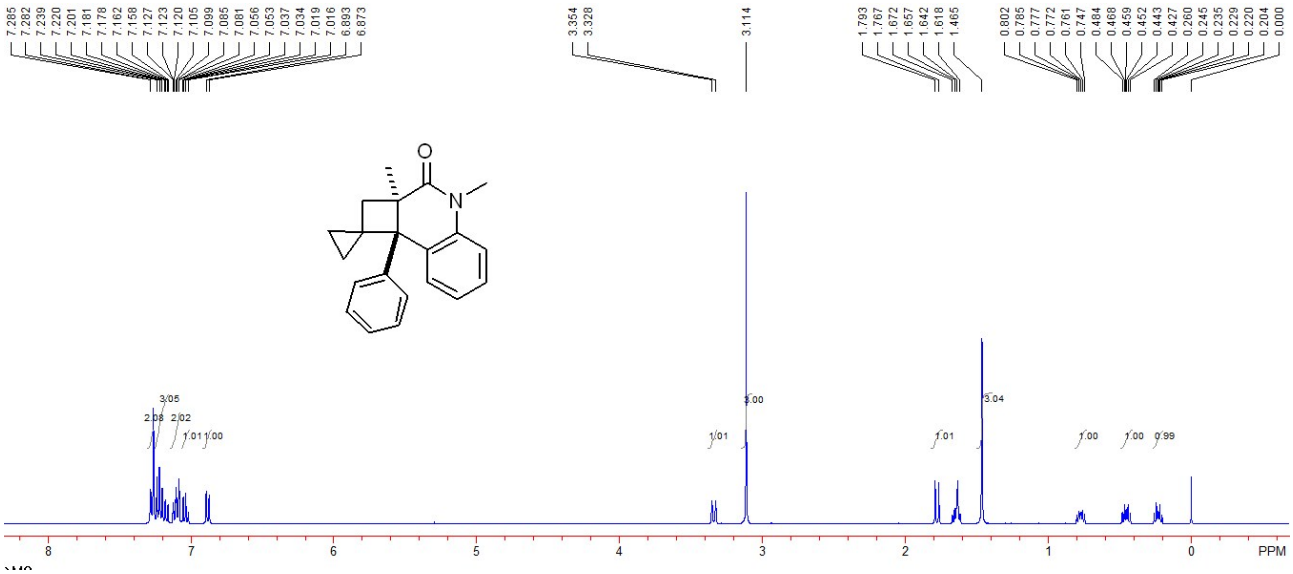
Compound **1** (0.20 mmol) was added to a sealed tube with a magnetic stir bar. *o*-$PhCl_2$ (2.0 mL) was added and the reaction tube was heated to 240 °C for 4 h under N_2 atmosphere. The reaction mixture was concentrated in vacuum, and the resulting residue was purified by a silica gel chromatography (eluent: petroleum ether / ethyl acetate = 10:1) to afford the desired product **3**.

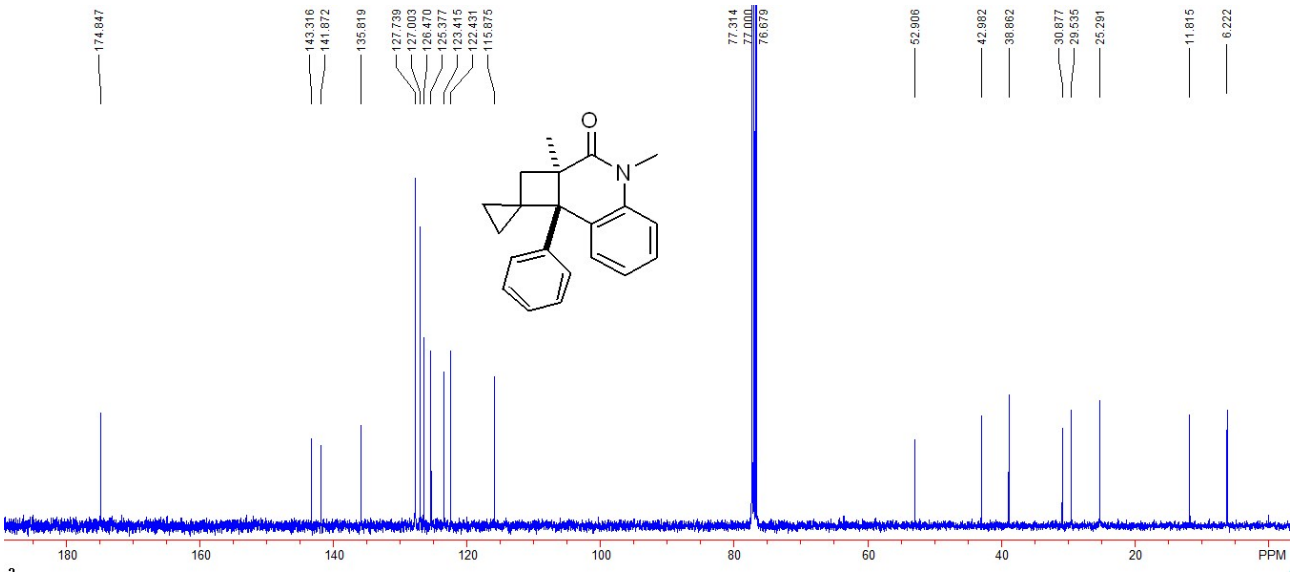
3. The Characterization Data of Products.

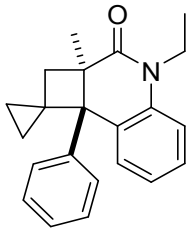


***anti*-2a,4-Dimethyl-8b-phenyl-2,2a,4,8b-tetrahydro-3*H*-spiro[cyclobuta[*c*]quinoline-1,1'-cyclopropan]-3-one (2a)**

pale green solid, 50 mg, 82% yield; *dr* > 20:1; m. p. 178 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.29-7.28 (m, 2H), 7.24-7.16 (m, 3H), 7.13-7.08 (m, 2H), 7.04 (td, J_2 = 7.6 Hz, J_1 = 1.2 Hz, 1H), 6.88 (d, J = 8.0 Hz, 1H), 3.34 (d, J = 10.4 Hz, 1H), 3.11 (s, 3H), 1.78 (d, J = 10.4 Hz, 1H), 1.67-1.62 (m, 1H), 1.47 (s, 3H), 0.80-0.75 (m, 1H), 0.46 (dt, J_1 = 6.0 Hz, J_2 = 10.0 Hz, 1H), 0.23 (dt, J_1 = 6.0 Hz, J_2 = 10.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 174.8, 143.3, 141.9, 135.8, 127.7, 127.0, 126.5, 125.4, 123.4, 122.4, 115.9, 52.9, 43.0, 38.9, 30.9, 29.5, 25.3, 11.8, 6.2; IR (CH_2Cl_2): 2987, 2929, 1680, 1656, 1597, 1496, 1451, 1396, 1352, 1280, 1250, 1224, 1099, 1084, 1043, 1023, 928, 918, 838, 769, 752, 718, 706, 681, 668, 658 cm^{-1}; HRMS (ESI) Calcd. For $C_{21}H_{22}NO$ $(M+H)^+$ requires: 304.1696, Found: 304.1691.

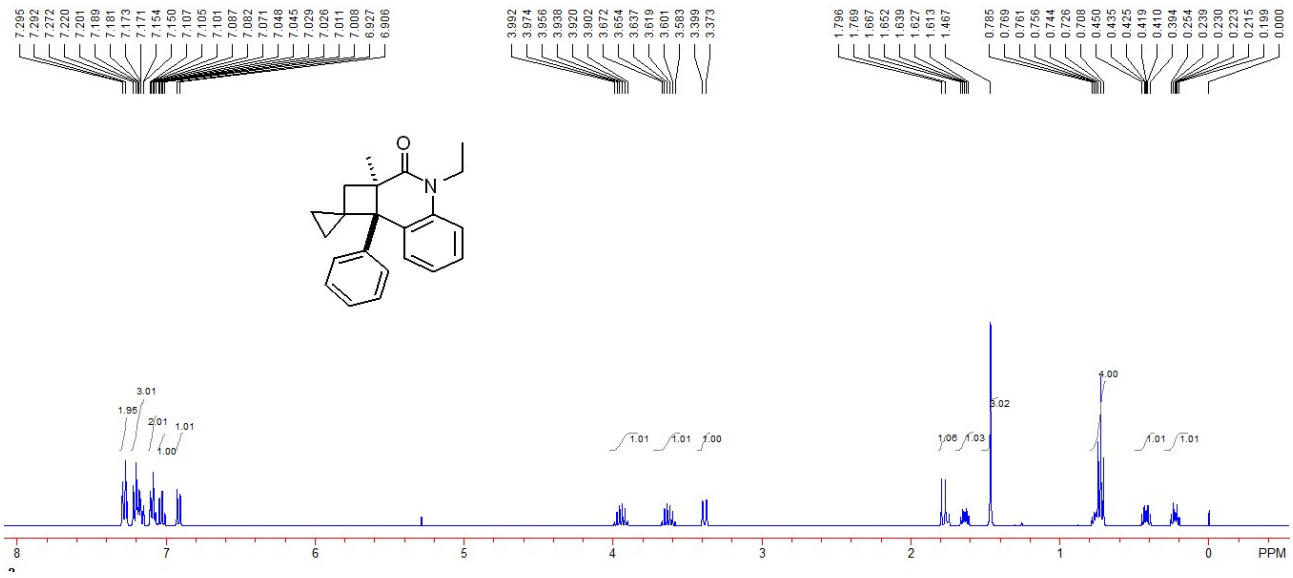


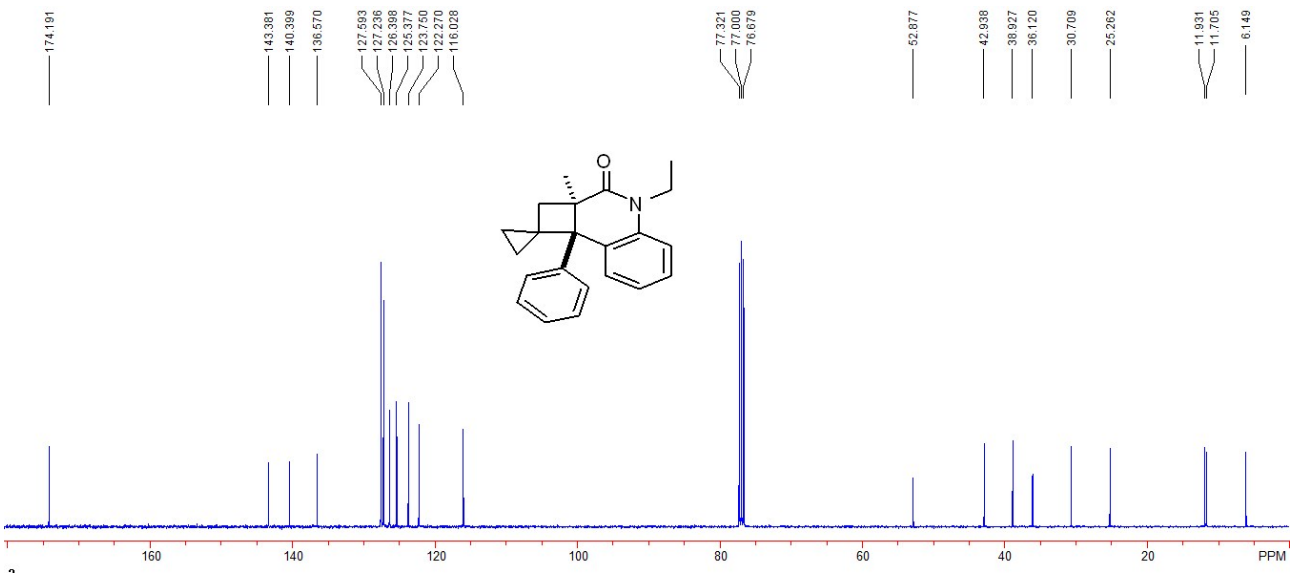


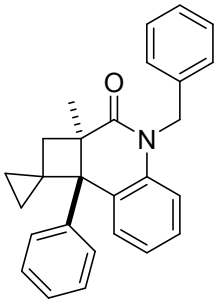


anti-4-Ethyl-2a-methyl-8b-phenyl-2,2a,4,8b-tetrahydro-3*H*-spiro[cyclobuta[*c*]quinoline-1,1'-cyclopropan]-3-one (2b)

pale green solid, 53 mg, 84% yield; *dr* > 20:1; m. p. 180 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.30-7.27 (m, 2H), 7.22-7.15 (m, 3H), 7.11-7.07 (m, 2H), 7.03 (td, J_2 = 7.6 Hz, J_1 = 1.2 Hz, 1H), 6.92 (d, J = 8.4 Hz, 1H), 3.99-3.90 (m, 1H), 3.67-3.58 (m, 1H), 3.39 (d, J = 10.4 Hz, 1H), 1.78 (d, J = 10.8 Hz, 1H), 1.67-1.63 (m, 1H), 1.47 (s, 3H), 0.79-0.71 (m, 4H), 0.42 (dt, J_1 = 6.0 Hz, J_2 = 10.0 Hz, 1H), 0.23 (dt, J_1 = 6.0 Hz, J_2 = 10.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 174.2, 143.4, 140.4, 136.6, 127.6, 127.2, 126.4, 125.4, 123.8, 122.3, 116.0, 52.9, 42.9, 38.9, 36.1, 30.7, 25.3, 11.9, 11.7, 6.1; IR (CH_2Cl_2): 2972, 2930, 1667, 1609, 1494, 1423, 1349, 1329, 1225, 1193, 1026, 1009, 1000, 876, 834, 778, 756, 736, 702, 649 cm^{-1}; HRMS (ESI) Calcd. For $C_{22}H_{24}NO$ $(M+H)^+$ requires: 318.1852, Found: 318.1847.



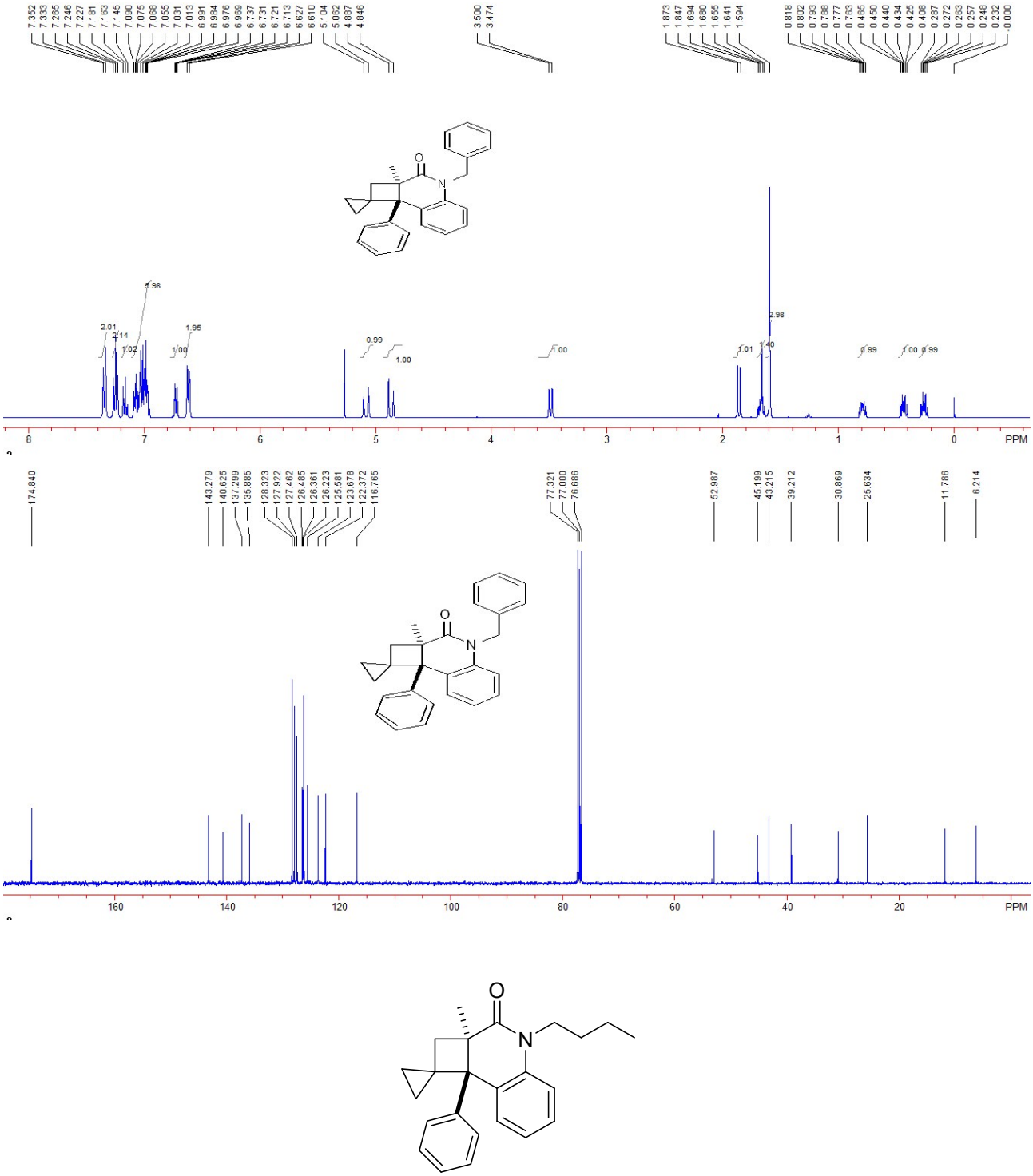




anti-4-Benzyl-2a-methyl-8b-phenyl-2,2a,4,8b-tetrahydro-3_H_-spiro[cyclobuta[_c_]quinoline-1,1'-cyclopropan]-3-one (2c)

pale green solid, 66 mg, 87% yield; *dr* > 20:1; m. p. 198 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.34 (d, *J* = 7.6 Hz, 2H), 7.25 (t, *J* = 7.6 Hz, 2H), 7.18-7.14 (m, 1H), 7.09-6.97 (m, 6H), 6.74-6.71 (m, 1H), 6.62 (d, *J* = 6.8 Hz, 2H), 5.08 (d, *J* = 16.8 Hz, 1H), 4.87 (d, *J* = 16.4 Hz, 1H), 3.49 (d, *J* = 10.4 Hz, 1H), 1.86 (d, *J* = 10.4 Hz, 1H), 1.69-1.64 (m, 1H), 1.59 (s, 3H), 0.82-0.76 (m, 1H), 0.44

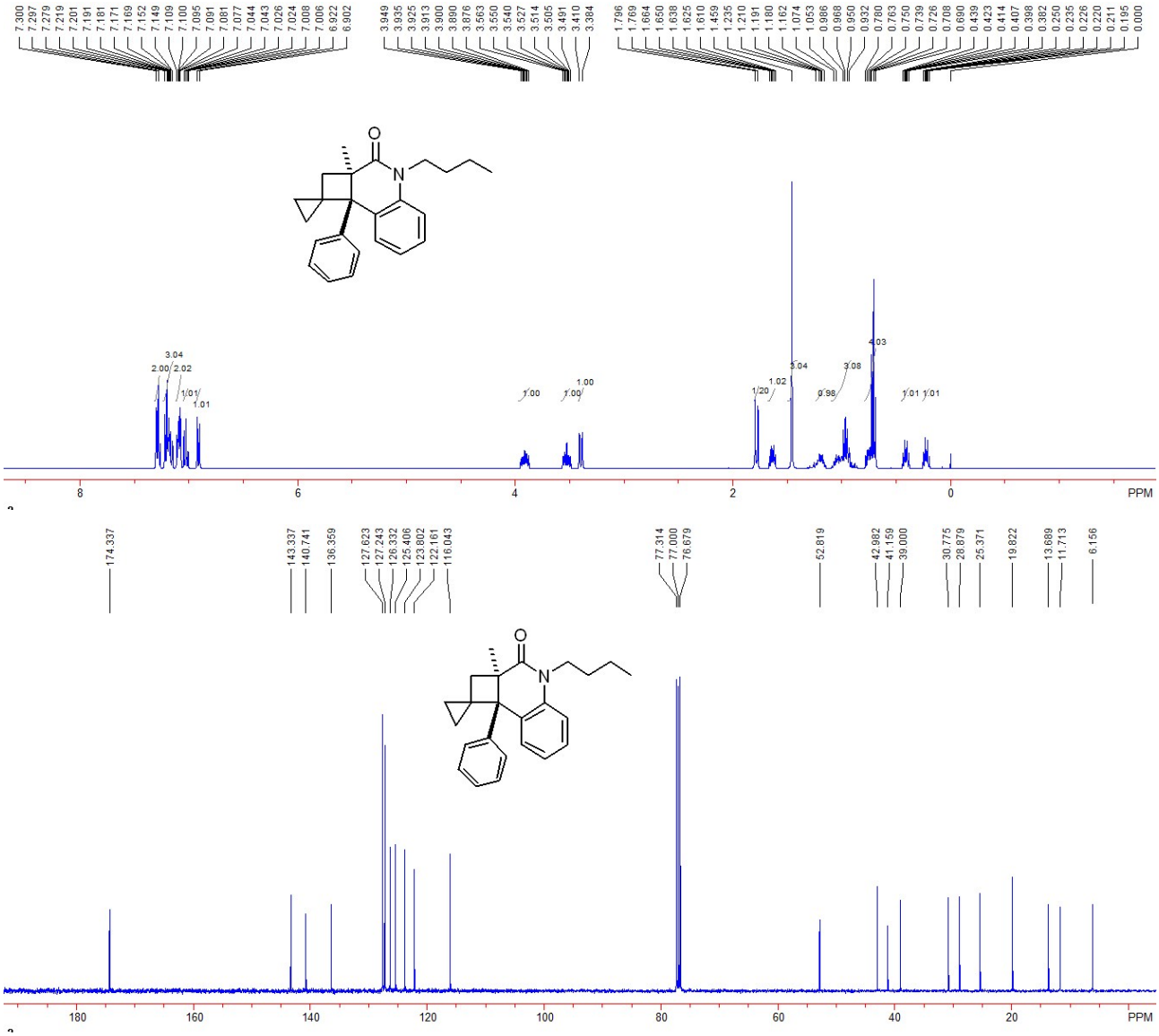
(dt, J_1 = 6.0 Hz, J_2 = 10.0 Hz, 1H), 0.26 (dt, J_1 = 6.0 Hz, J_2 = 10.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 174.8, 143.3, 140.6, 137.3, 135.9, 128.3, 127.9, 127.5, 126.5, 126.4, 126.2, 125.6, 123.7, 122.4, 116.8, 53.0, 45.2, 43.2, 39.2, 30.9, 25.6, 11.8, 6.2; IR (CH_2Cl_2): 2971, 2926, 1649, 1596, 1495, 1453, 1369, 1320, 1275, 1183, 1066, 1078, 1057, 1024, 1007, 753, 745, 736, 702, 669 cm^{-1}; HRMS (ESI) Calcd. For $C_{27}H_{26}NO$ $(M+H)^+$ requires: 380.2009, Found: 380.2001.

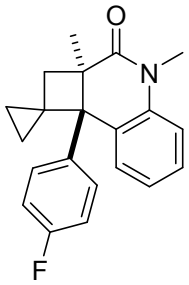


***anti*-4-Butyl-2a-methyl-8b-phenyl-2,2a,4,8b-tetrahydro-3*H*-spiro[cyclobuta[*c*]quinoline-1,1'-**

cyclopropan]-3-one (2d)

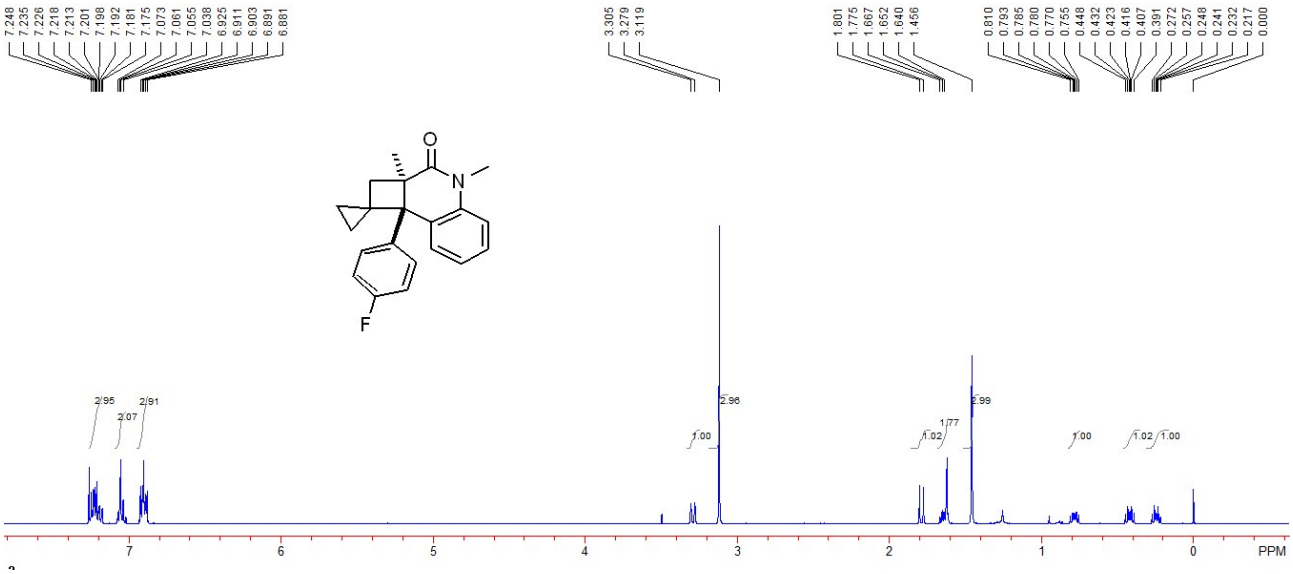
pale green solid, 60 mg, 86% yield; *dr* > 20:1; m. p. 190 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.30-7.28 (m, 2H), 7.22-7.15 (m, 3H), 7.11-7.08 (m, 2H), 7.03 (td, J_2 = 7.6 Hz, J_1 = 0.8 Hz, 1H), 6.91 (d, J = 8.0 Hz, 1H), 3.95-3.88 (m, 1H), 3.56-3.49 (m, 1H), 3.40 (d, J = 10.4 Hz, 1H), 1.78 (d, J = 10.8 Hz, 1H), 1.66-1.61 (m, 1H), 1.46 (s, 3H), 1.24-1.16 (m, 1H), 1.07-0.93 (m, 3H), 0.78-0.69 (m, 4H), 0.41 (dt, J_1 = 6.4 Hz, J_2 = 10.0 Hz, 1H), 0.22 (dt, J_1 = 6.0 Hz, J_2 = 10.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 174.3, 143.3, 140.7, 136.4, 127.6, 127.2, 126.3, 125.4, 123.8, 122.2, 116.0, 52.8, 43.0, 41.2, 39.0, 30.8, 28.9, 25.4, 19.8, 13.7, 11.7, 6.2; IR (CH_2Cl_2): 2958, 2931, 1677, 1452, 1370, 1353, 1299, 1104, 1080, 1049, 756, 717, 705 cm^{-1}; HRMS (ESI) Calcd. For $C_{24}H_{28}NO$ $(M+H)^+$ requires: 346.2165, Found: 346.2159.

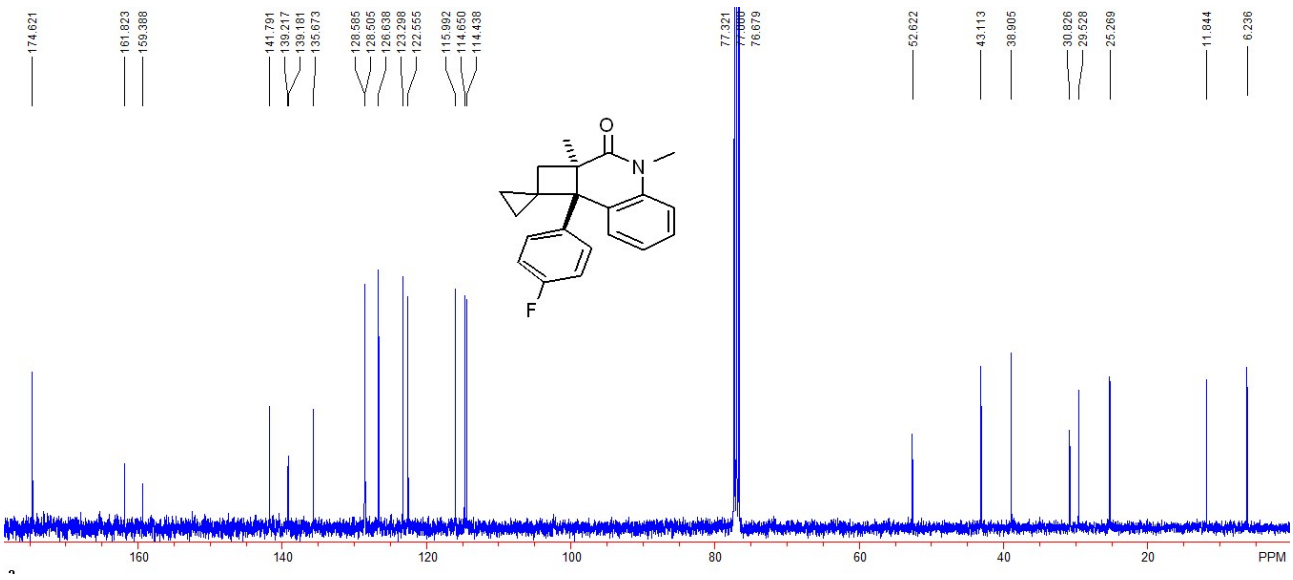


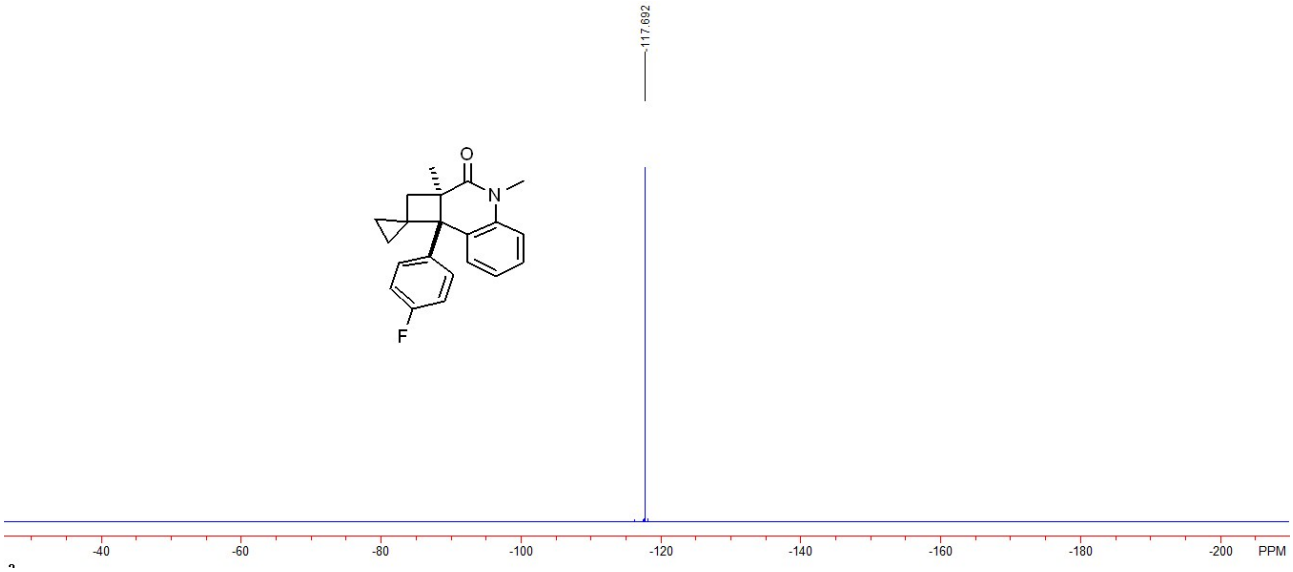


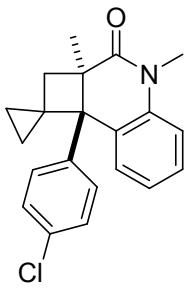
***anti*-8b-(4-fluorophenyl)-2a,4-Dimethyl-2,2a,4,8b-tetrahydro-3*H*-spiro[cyclobuta[*c*]quinoline-1,1'-cyclopropan]-3-one (2e)**

pale green solid, 49 mg, 77% yield; *dr* > 20:1; m. p. 167 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.25-7.18 (m, 3H), 7.07-7.04 (m, 2H), 6.93-6.88 (m, 3H), 3.29 (d, J = 10.4 Hz, 1H), 3.12 (s, 3H), 1.79 (d, J = 10.4 Hz, 1H), 1.67-1.64 (m, 1H), 1.46 (s, 3H), 0.81-0.76 (m, 1H), 0.42 (dt, J_1 = 6.4 Hz, J_2 = 10.0 Hz, 1H), 0.24 (dt, J_1 = 6.0 Hz, J_2 = 10.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 174.6, 160.6 (d, J = 243.5 Hz), 141.8, 139.2 (d, J = 3.6 Hz), 135.7, 128.5 (d, J = 8.0 Hz), 126.6, 123.3, 122.6, 116.0, 114.5 (d, J = 21.2 Hz), 52.6, 43.1, 38.9, 30.8, 29.5, 25.3, 11.8, 6.2; ^{19}F NMR (376 MHz, $CDCl_3$): δ -117.7; IR (CH_2Cl_2): 2971, 2928, 1655, 1597, 1492, 1453, 1367, 1279, 1218, 824, 753, 734 cm^{-1}; HRMS (ESI) Calcd. For $C_{21}H_{21}FNO$ $(M+H)^+$ requires: 322.1602, Found: 322.1595.





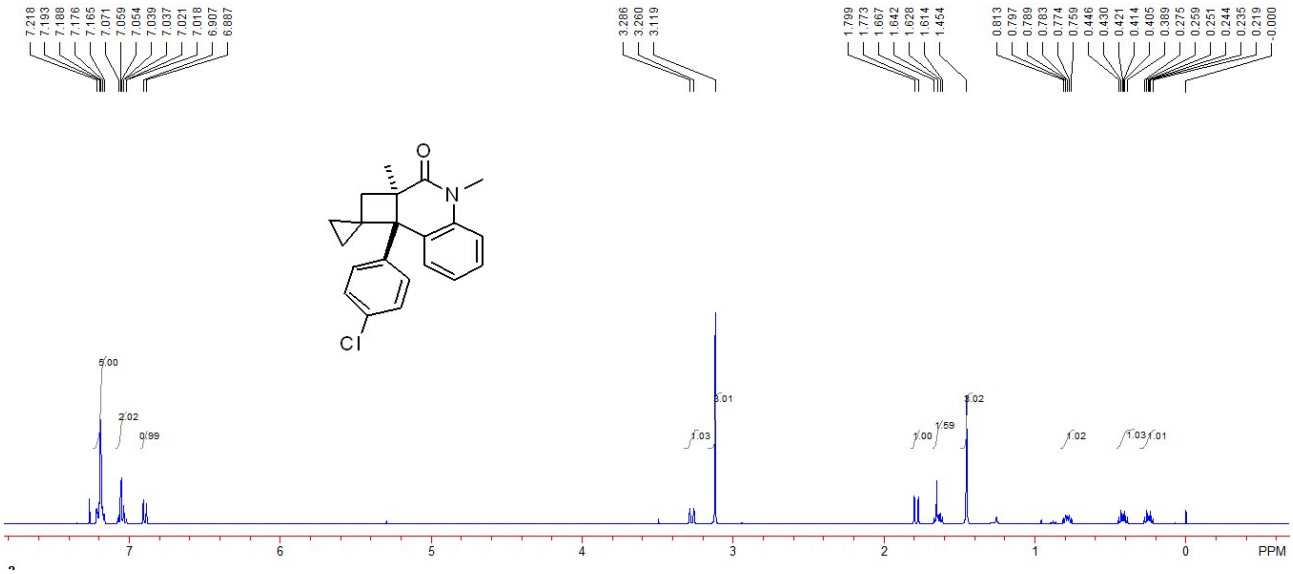


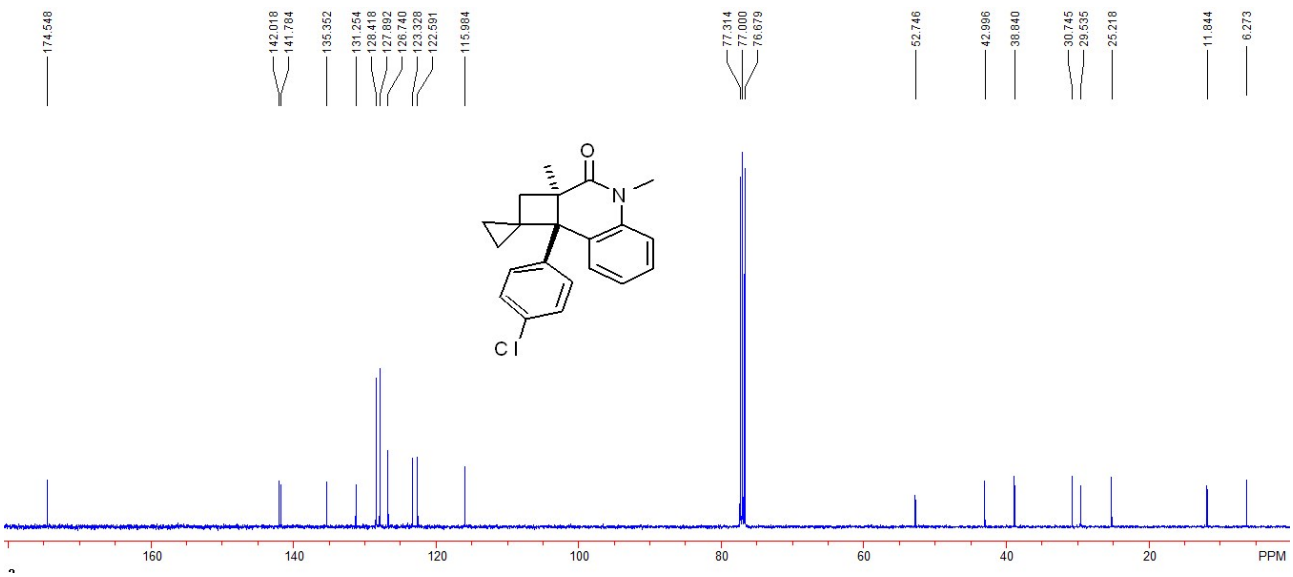


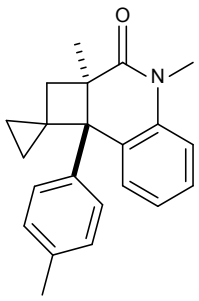
***anti*-8b-(4-chlorophenyl)-2a,4-Dimethyl-2,2a,4,8b-tetrahydro-3*H*-spiro[cyclobuta[*c*]quinoline-1,1'-cyclopropan]-3-one (2f)**

pale green solid, 53 mg, 79% yield; *dr* > 20:1; m. p. 189 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.22-7.17 (m, 5H), 7.07-7.02 (m, 2H), 6.90 (d, J = 8.0 Hz, 1H), 3.27 (d, J = 10.4 Hz, 1H), 3.12 (s, 3H), 1.79 (d, J = 10.4 Hz, 1H), 1.67-1.61 (m, 1H), 1.45 (s, 3H), 0.79 (dt, J_1 = 6.0 Hz, J_2 = 10.0 Hz, 1H), 0.42 (dt, J_1 = 6.4 Hz, J_2 = 10.0 Hz, 1H), 0.25 (dt, J_1 = 6.4 Hz, J_2 = 9.6 Hz, 1H); ^{13}C NMR (100

MHz, $CDCl_3$, TMS) δ 174.5, 142.0, 141.8, 135.4, 131.3, 128.4, 127.9, 126.7, 123.3, 122.6, 116.0, 52.7, 43.0, 38.8, 30.7, 29.5, 25.2, 11.8, 6.3; IR (CH_2Cl_2): 2965, 2928, 1686, 1598, 1494, 1465, 1371, 1279, 1245, 1096, 1043, 1033, 1023, 853, 757, 734, 729 cm^{-1}; HRMS (ESI) Calcd. For $C_{21}H_{21}ClNO$ $(M+H)^+$ requires: 338.1306, Found: 338.1302.

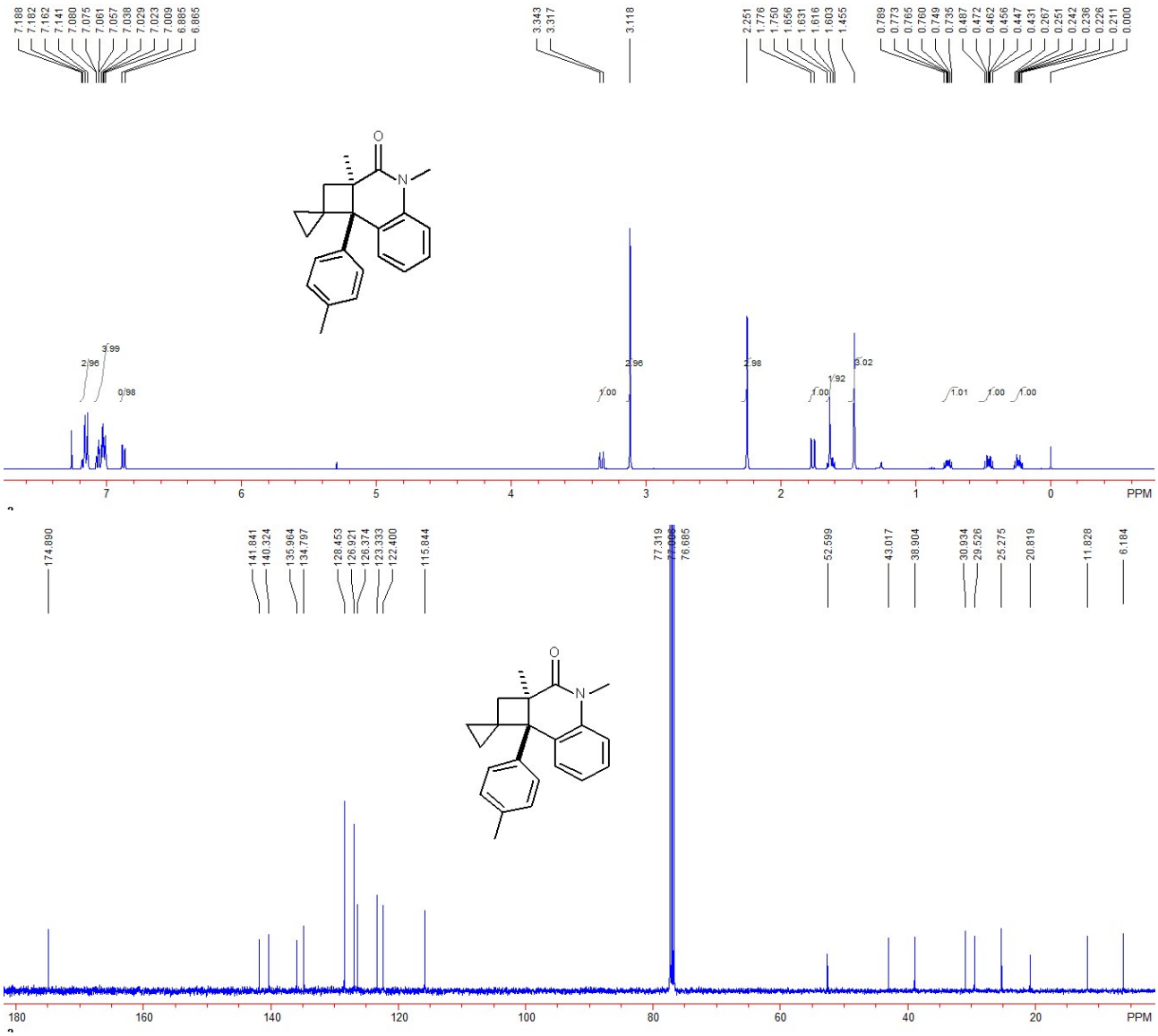


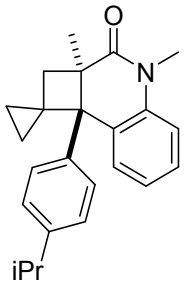




anti-2a,4-Dimethyl-8b-(p-tolyl)-2,2a,4,8b-tetrahydro-3*H*-spiro[cyclobuta[*c*]quinoline-1,1'-cyclopropan]-3-one (2g)

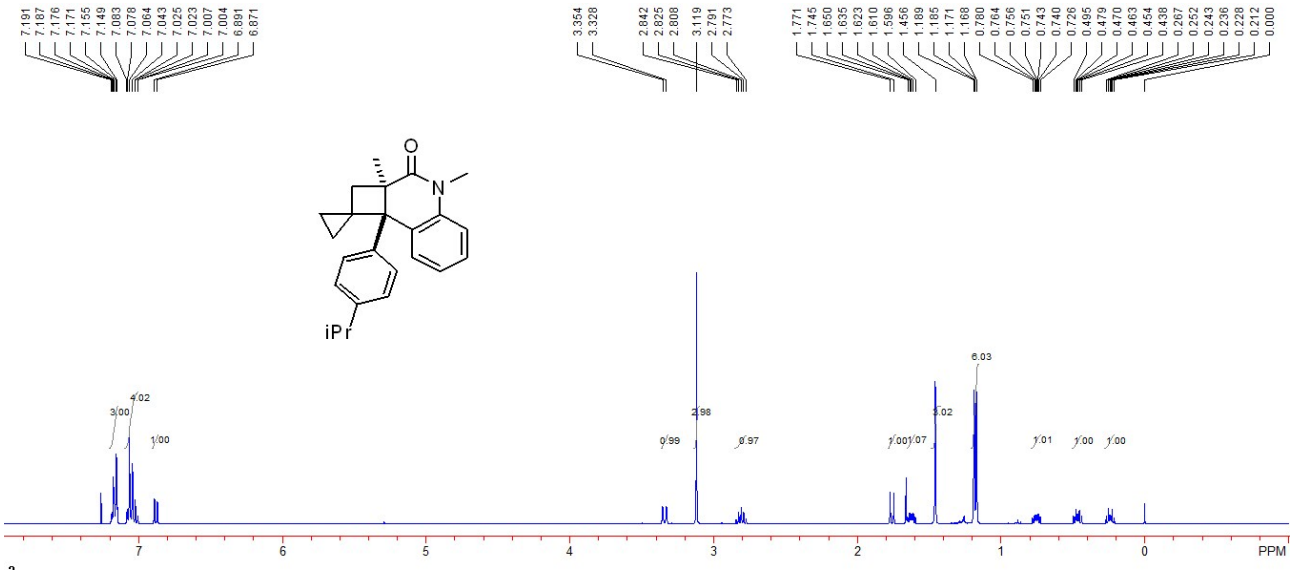
pale green solid, 51 mg, 80% yield; *dr* > 20:1; m. p. 170 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.19-7.14 (m, 3H), 7.08-7.01 (m, 4H), 6.88 (d, J = 8.0 Hz, 1H), 3.33 (d, J = 10.4 Hz, 1H), 3.12 (s, 3H), 2.25 (s, 3H), 1.76 (d, J = 10.4 Hz, 1H), 1.66-1.60 (m, 1H), 1.46 (s, 3H), 0.79-0.74 (m, 1H), 0.46 (dt, J_1 = 6.0 Hz, J_2 = 10.0 Hz, 1H), 0.24 (dt, J_1 = 6.0 Hz, J_2 = 10.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 174.9, 141.8, 140.3, 136.0, 134.8, 128.5, 126.9, 126.4, 123.3, 122.4, 115.8, 52.6, 43.0, 38.9, 30.9, 29.5, 25.3, 20.8, 11.8, 6.2; IR (CH_2Cl_2): 2964, 2926, 1682, 1455, 1370, 1349, 1319, 1278, 1248, 1227, 1097, 1043, 1022, 926, 815, 754, 740, 730, 653 cm^{-1}; HRMS (ESI) Calcd. For $C_{22}H_{24}NO$ $(M+H)^+$ requires: 318.1852, Found: 318.1846.

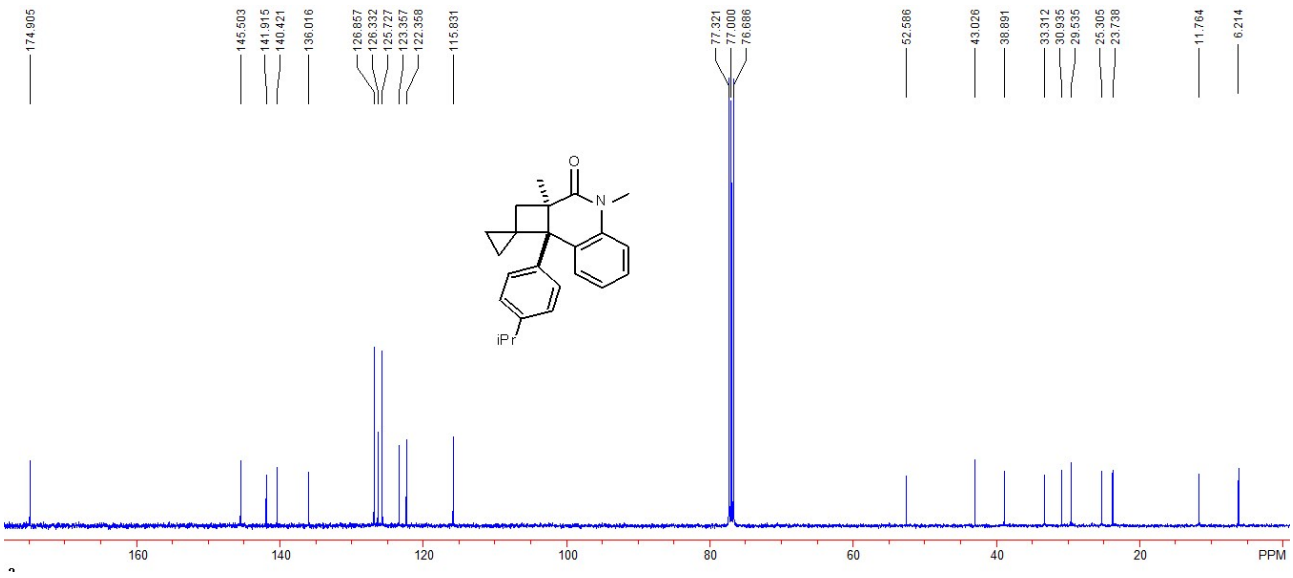


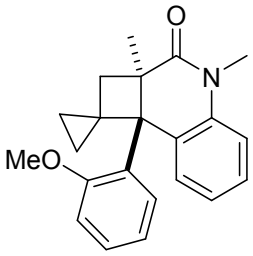


***anti*-8b-(4-isopropylphenyl)-2a,4-Dimethyl-2,2a,4,8b-tetrahydro-3*H*-spiro[cyclobuta[*c*]quinoline-1,1'-cyclopropan]-3-one (2h)**

pale green solid, 59 mg, 84% yield; *dr* > 20:1; m. p. 180 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.19-7.15 (m, 3H), 7.08-7.00 (m, 4H), 6.88 (d, J = 8.0 Hz, 1H), 3.34 (d, J = 10.4 Hz, 1H), 3.12 (s, 3H), 2.84-2.77 (m, 1H), 1.76 (d, J = 10.4 Hz, 1H), 1.65-1.60 (m, 1H), 1.46 (s, 3H), 1.18 (dd, J_1 = 1.2 Hz, J_2 = 7.2 Hz, 6H), 0.78-0.73 (m, 1H), 0.47 (dt, J_1 = 6.0 Hz, J_2 = 10.0 Hz, 1H), 0.24 (dt, J_1 = 6.0 Hz, J_2 = 10.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 174.9, 145.5, 141.9, 140.4, 136.0, 126.9, 126.3, 125.7, 123.4, 122.4, 115.8, 52.6, 43.0, 38.9, 33.3, 30.9, 29.5, 25.3, 23.7, 11.8, 6.2; IR (CH_2Cl_2): 2954, 2930, 1684, 1455, 1371, 1350, 1316, 1276, 1247, 1225, 1093, 1077, 1056, 1042, 1029, 1021, 1012, 922, 892, 823, 754, 714, 672 cm^{-1}; HRMS (ESI) Calcd. For $C_{24}H_{28}NO$ $(M+H)^+$ requires: 346.2165, Found: 346.2160.

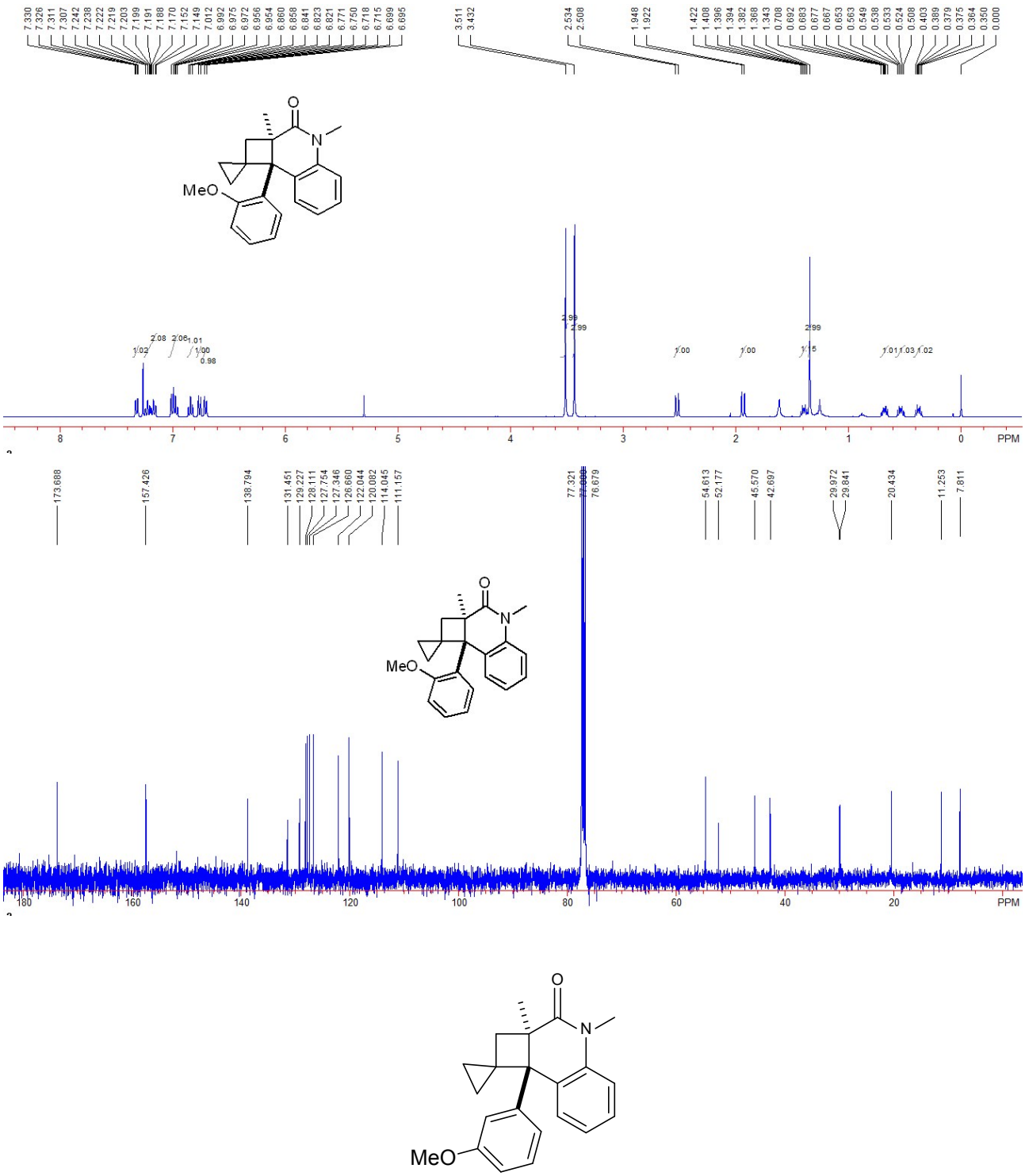






anti-8b-(2-methoxyphenyl)-2a,4-Dimethyl-2,2a,4,8b-tetrahydro-3*H*-spiro[cyclobuta[*c*]quinoline-1,1'-cyclopropan]-3-one (2j)

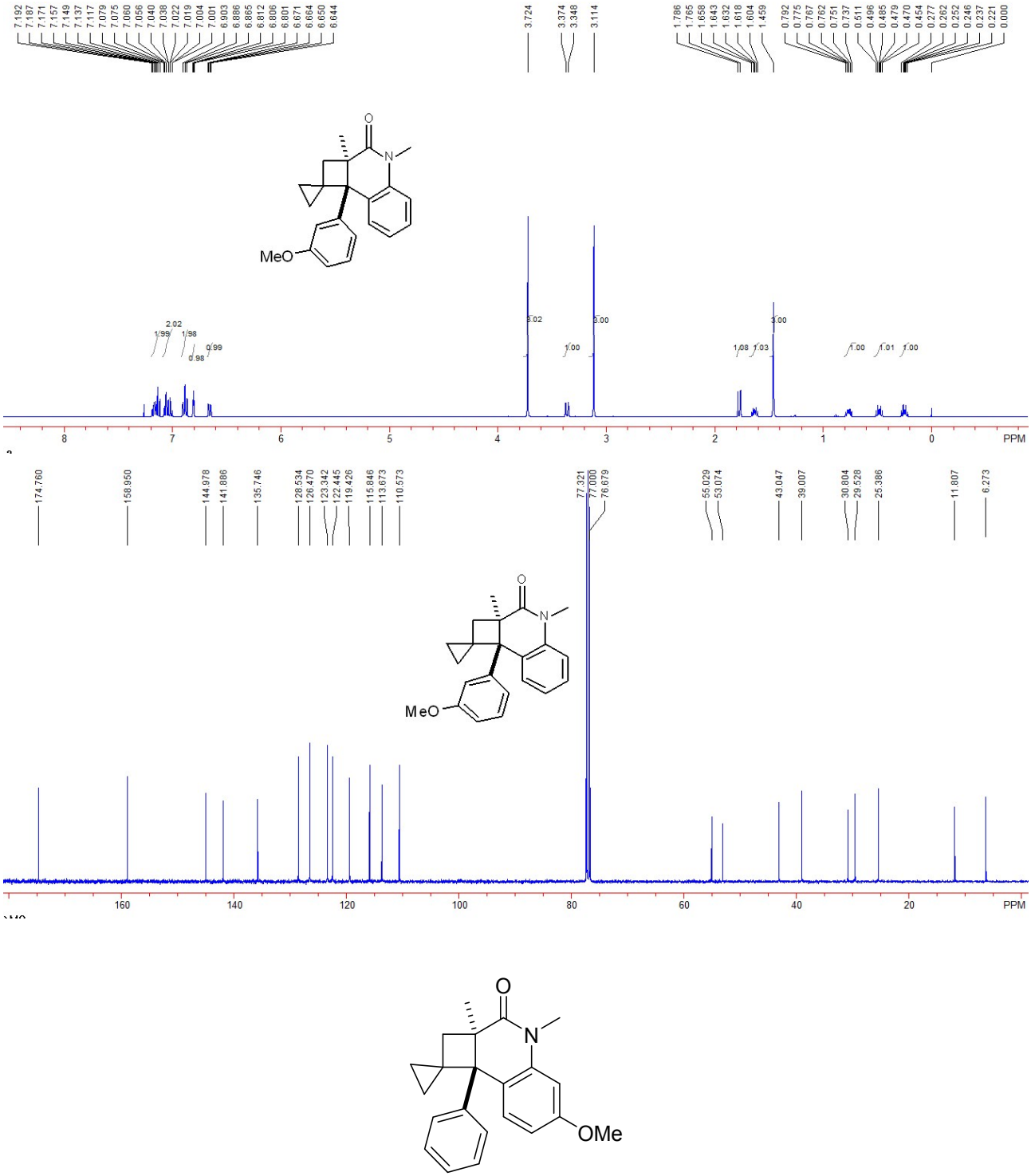
pale green solid, 34 mg, 50% yield; *dr* > 20:1; m. p. 175 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.32 (dd, J_2 = 7.6 Hz, J_1 = 1.2 Hz, 1H), 7.24-7.15 (m, 2H), 7.01-6.95 (m, 2H), 6.86-6.82 (m, 1H), 6.76 (d, J = 8.4 Hz, 1H), 6.71 (dd, J_2 = 7.6 Hz, J_1 = 1.2 Hz, 1H), 3.51 (s, 3H), 3.43 (s, 3H), 2.52 (d, J = 10.4 Hz, 1H), 1.94 (d, J = 10.4 Hz, 1H), 1.42-1.37 (m, 1H), 1.34 (s, 3H), 0.68 (dt, J_1 = 6.0 Hz, J_2 = 10.0 Hz, 1H), 0.56-0.51 (m, 1H), 0.40-0.35 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 173.7, 157.4, 138.8, 131.5, 129.2, 128.1, 127.8, 127.3, 126.7, 122.0, 120.1, 114.0, 111.2, 54.6, 52.2, 45.6, 42.7, 30.0, 29.8, 20.4, 11.3, 7.8; IR (CH_2Cl_2): 2988, 2926, 1659, 1596, 1503, 1488, 1467, 1416, 1361, 1297, 1254, 1088, 1061, 1031, 851, 803, 758, 748, 705, 668 cm^{-1}; HRMS (ESI) Calcd. For $C_{22}H_{24}NO_2$ $(M+H)^+$ requires: 334.1802, Found: 334.1795.



***anti*-8b-(3-methoxyphenyl)-2a,4-Dimethyl-2,2a,4,8b-tetrahydro-3*H*-spiro[cyclobuta[*c*]quinoline-1,1'-cyclopropan]-3-one (2k)**

pale green solid, 48 mg, 72% yield; *dr* > 20:1; m. p. 178 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.19-7.12 (m, 2H), 7.08-7.00 (m, 2H), 6.90-6.87 (m, 2H), 6.81-6.60 (m, 1H), 6.67-6.64 (m, 1H), 3.72 (s, 3H), 3.36 (d, J = 10.4 Hz, 1H), 3.11 (s, 3H), 1.78 (d, J = 10.4 Hz, 1H), 1.66-1.60 (m, 1H), 1.46 (s, 3H), 0.76 (dt, J_1 = 6.0 Hz, J_2 = 10.0 Hz, 1H), 0.48 (dt, J_1 = 6.4 Hz, J_2 = 10.0 Hz, 1H), 0.25

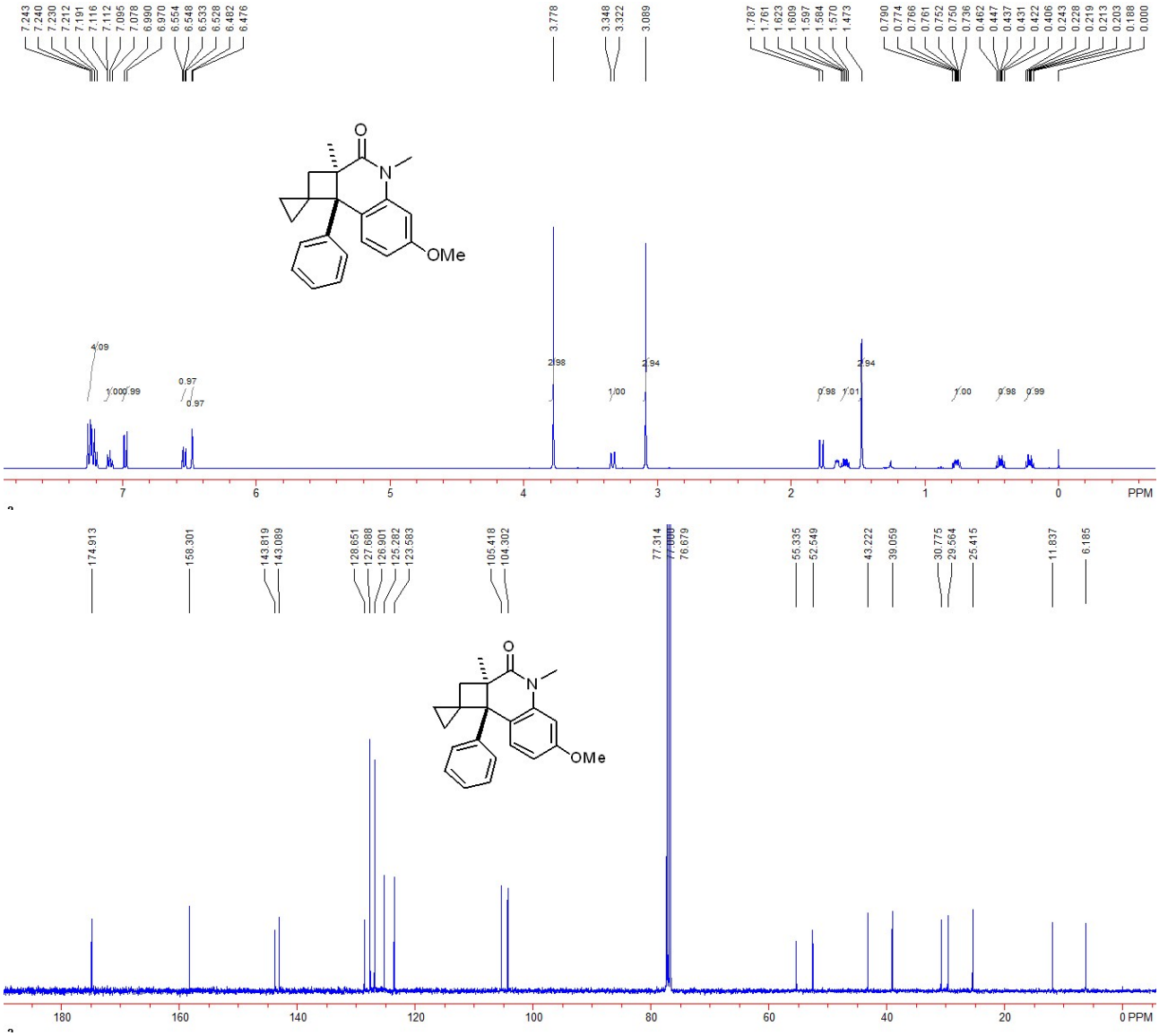
(dt, J_1 = 6.0 Hz, J_2 = 10.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 174.8, 159.0, 145.0, 141.9, 135.7, 128.5, 126.5, 123.3, 122.4, 119.4, 115.8, 113.7, 110.6, 55.0, 53.1, 43.0, 39.0, 30.8, 29.5, 25.4, 11.8, 6.3; IR (CH_2Cl_2): 2975, 1683, 1603, 1454, 1431, 1323, 1310, 1297, 1277, 1238, 1226, 1198, 1095, 1077, 1040, 942, 905, 799, 752, 739, 724, 701, 678 cm^{-1}; HRMS (ESI) Calcd. For $C_{22}H_{24}NO_2$ $(M+H)^+$ requires: 334.1802, Found: 334.1795.

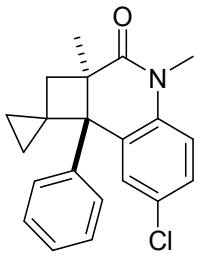


***anti*-6-Methoxy-2a,4-dimethyl-8b-phenyl-2,2a,4,8b-tetrahydro-3*H*-**

spiro[cyclobuta[*c*]quinoline-1,1'-cyclopropan]-3-one (2l)

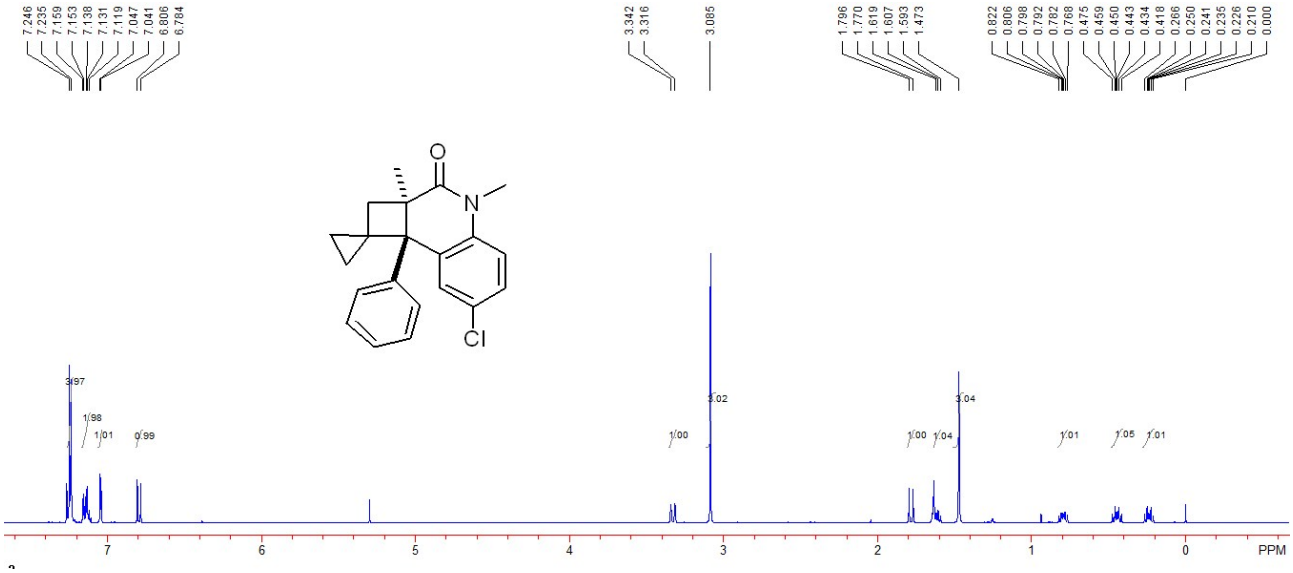
pale green solid, 55 mg, 82% yield; *dr* > 20:1; m. p. 175 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.24-7.19 (m, 4H), 7.12-7.08 (m, 1H), 6.98 (d, J = 8.0 Hz, 1H), 6.54 (dd, J_2 = 8.4 Hz, J_1 = 2.4 Hz, 1H), 6.48 (d, J = 2.4 Hz, 1H), 3.78 (s, 3H), 3.34 (d, J = 10.4 Hz, 1H), 3.09 (s, 3H), 1.77 (d, J = 10.4 Hz, 1H), 1.62-1.57 (m, 1H), 1.47 (s, 3H), 0.79-0.74 (m, 1H), 0.43 (dt, J_1 = 6.0 Hz, J_2 = 10.0 Hz, 1H), 0.22 (dt, J_1 = 6.0 Hz, J_2 = 10.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 174.9, 158.3, 143.8, 143.1, 128.7, 127.7, 126.9, 125.3, 123.6, 105.4, 104.3, 55.3, 52.5, 43.2, 39.1, 30.8, 29.6, 25.4, 11.8, 6.2; IR (CH_2Cl_2): 2951, 1682, 1615, 1577, 1468, 1443, 1297, 1279, 1253, 1234, 1183, 1092, 1076, 1043, 1035, 959, 934, 851, 803, 740, 734, 715, 705 cm^{-1}; HRMS (ESI) Calcd. For $C_{22}H_{24}NO_2$ $(M+H)^+$ requires: 334.1802, Found: 334.1796.

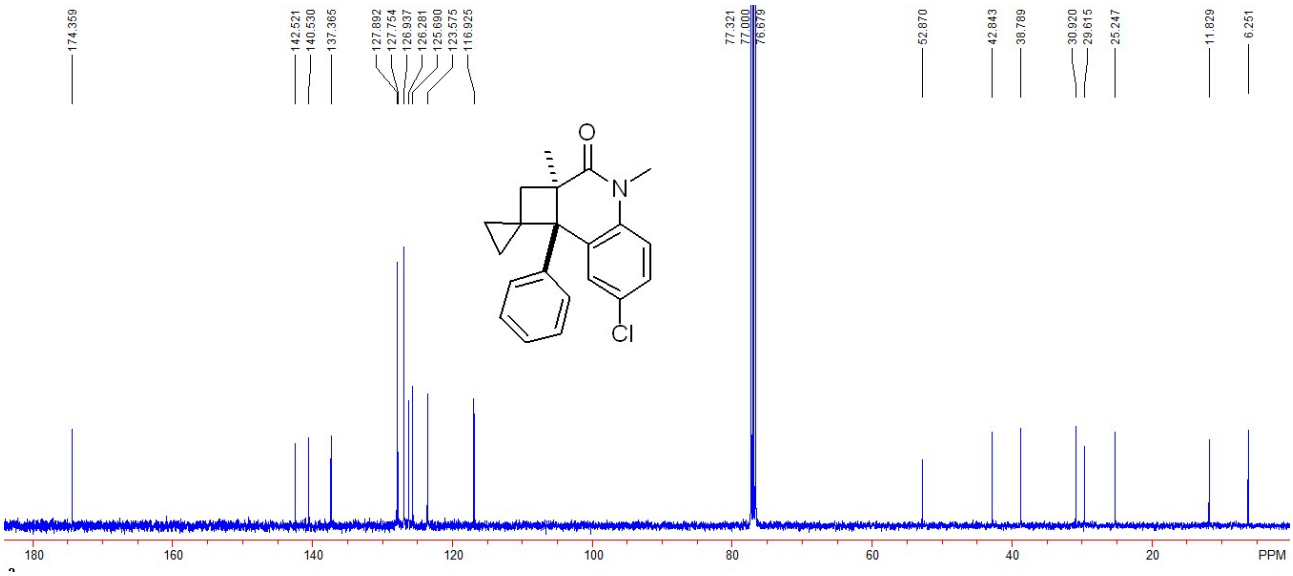


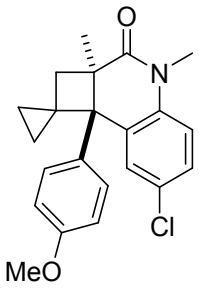


anti-7-Chloro-2a,4-dimethyl-8b-phenyl-2,2a,4,8b-tetrahydro-3_H_-spiro[cyclobuta[_c_]quinoline-1,1'-cyclopropan]-3-one (2m)

pale green solid, 57 mg, 84% yield; *dr* > 20:1; m. p. 180 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.24 (d, *J* = 4.4 Hz, 4H), 7.16-7.12 (m, 2H), 7.04 (d, *J* = 2.4 Hz, 1H), 6.80 (d, *J* = 8.8 Hz, 1H), 3.33 (d, *J* = 10.4 Hz, 1H), 3.09 (s, 3H), 1.78 (d, *J* = 10.4 Hz, 1H), 1.62-1.59 (m, 1H), 1.47 (s, 3H), 0.82-0.77 (m, 1H), 0.45 (dt, J_1 = 6.4 Hz, J_2 = 10.0 Hz, 1H), 0.24 (dt, J_1 = 6.0 Hz, J_2 = 10.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 174.4, 142.5, 140.5, 137.4, 127.9, 127.8, 126.9, 126.3, 125.7, 123.6, 116.9, 52.9, 42.8, 38.8, 30.9, 29.6, 25.2, 11.8, 6.3; IR (CH_2Cl_2): 2988, 2901, 1679, 1466, 1446, 1372, 1352, 1248, 1227, 1106, 1077, 1046, 817, 748, 703, 668 cm^{-1}; HRMS (ESI) Calcd. For $C_{21}H_{21}ClNO$ $(M+H)^+$ requires: 338.1306, Found: 338.1302.

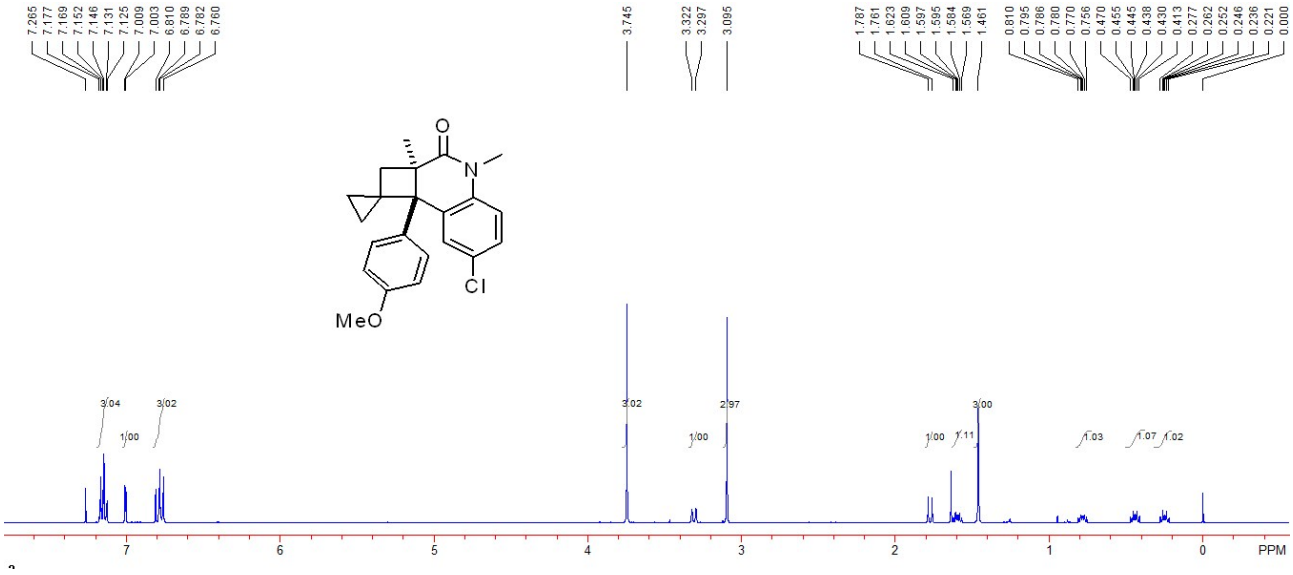


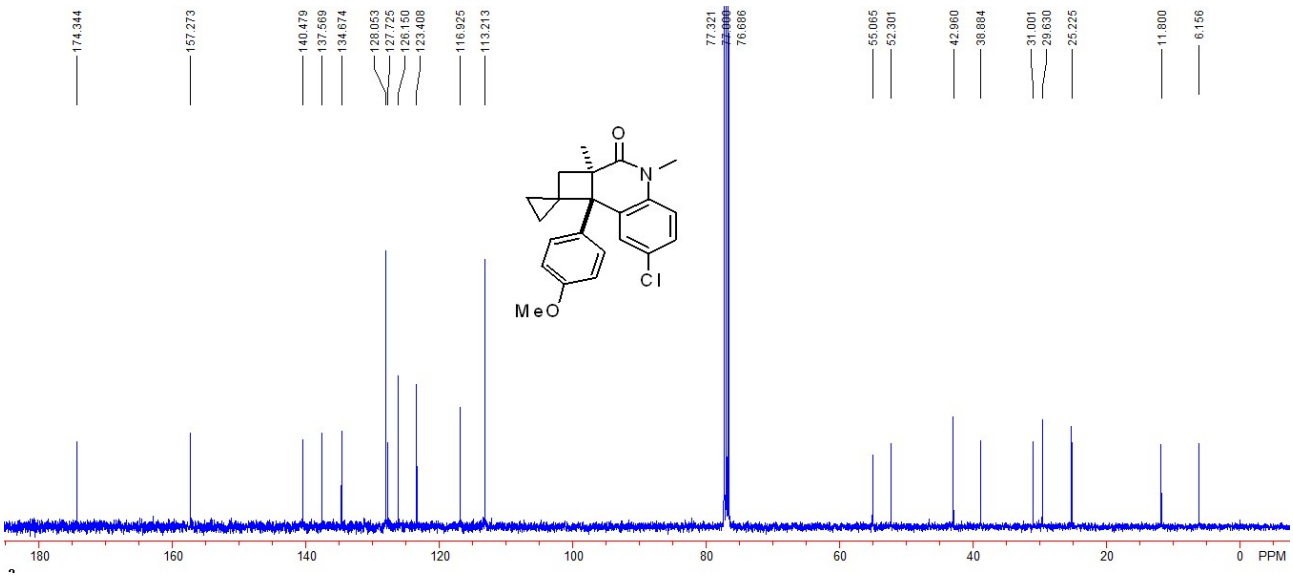


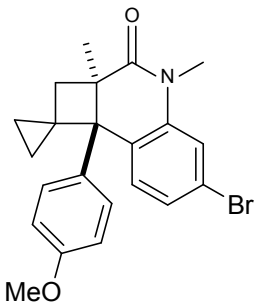


***anti*-7-Chloro-8b-(4-methoxyphenyl)-2a,4-dimethyl-2,2a,4,8b-tetrahydro-3*H*-spiro[cyclobuta[*c*]quinoline-1,1'-cyclopropan]-3-one (2n)**

pale green solid, 63 mg, 85% yield; *dr* > 20:1; m. p. 198 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.18-7.13 (m, 3H), 7.01 (d, J = 2.4 Hz, 1H), 6.81-6.76 (m, 3H), 3.75 (s, 3H), 3.31 (d, J = 10.0 Hz, 1H), 3.10 (s, 3H), 1.77 (d, J = 10.4 Hz, 1H), 1.60 (dt, J_1 = 6.0 Hz, J_2 = 10.0 Hz, 1H), 1.46 (s, 3H), 0.78 (dt, J_1 = 6.0 Hz, J_2 = 10.0 Hz, 1H), 0.47-0.41 (m, 1H), 0.25 (dt, J_1 = 6.0 Hz, J_2 = 10.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 174.3, 157.3, 140.5, 137.6, 134.7, 128.1, 127.7, 126.2, 123.4, 116.9, 113.2, 55.1, 52.3, 43.0, 38.9, 31.0, 29.6, 25.2, 11.8, 6.2; IR (CH_2Cl_2): 2972, 1683, 1606, 1509, 1465, 1373, 1275, 1250, 1035, 1028, 1021, 1012, 942, 865, 833, 794, 752, 669 cm^{-1}; HRMS (ESI) Calcd. For $C_{22}H_{23}ClNO$ $(M+H)^+$ requires: 368.1412, Found: 368.1407.



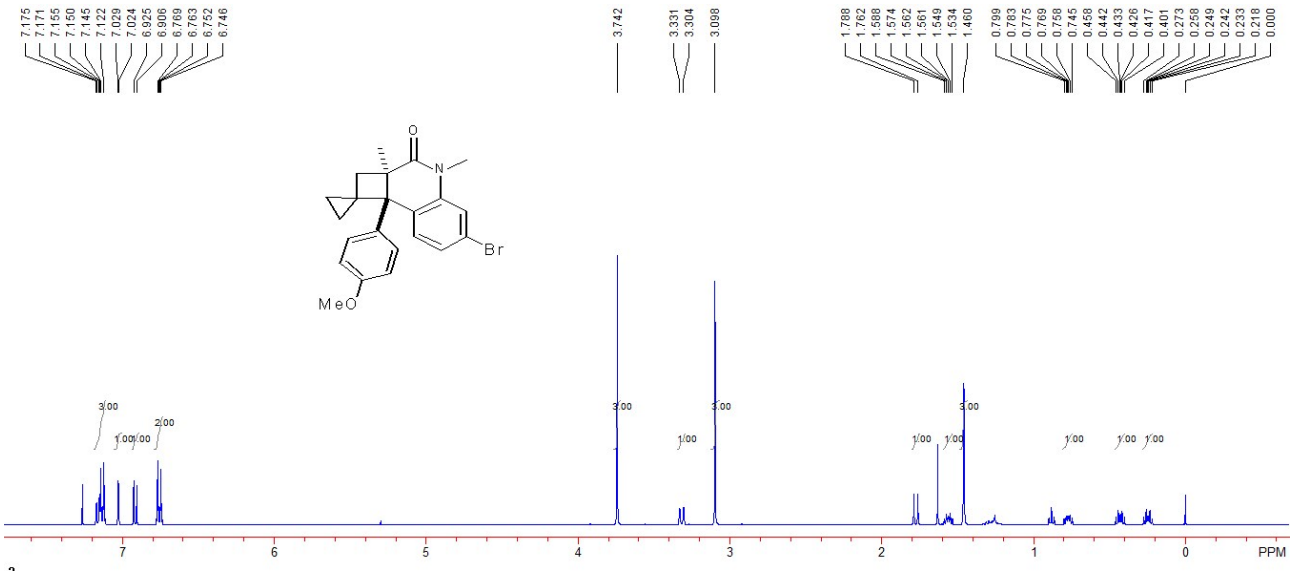


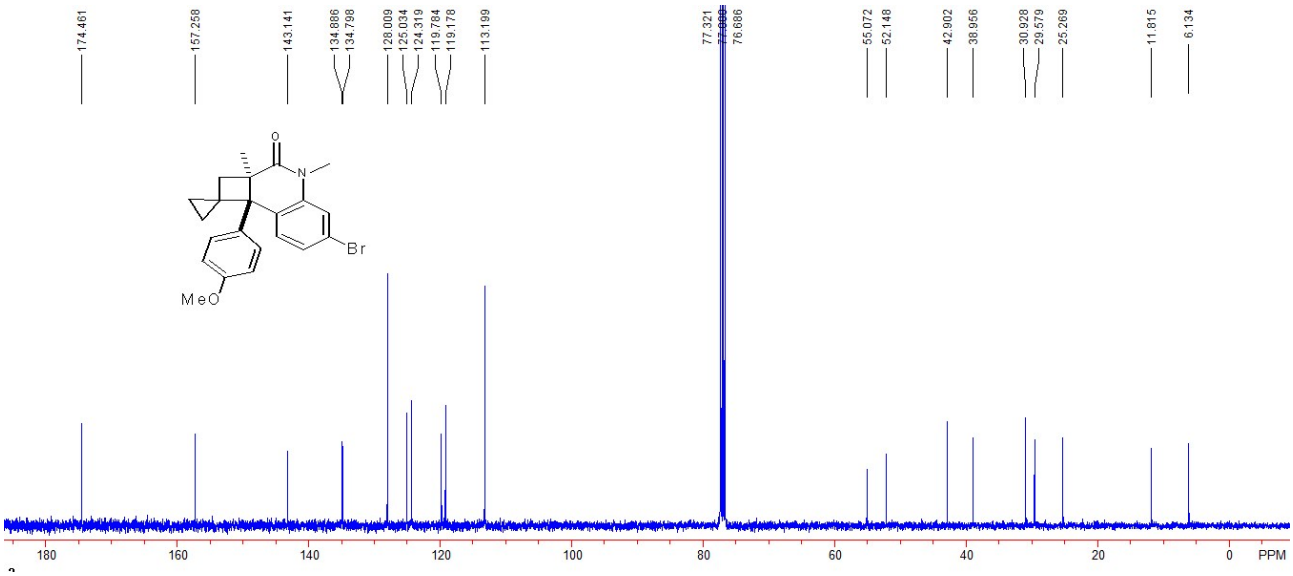


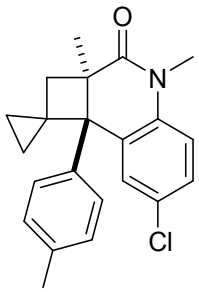
anti-6-Bromo-8b-(4-methoxyphenyl)-2a,4-dimethyl-2,2a,4,8b-tetrahydro-3*H*-spiro[cyclobuta[*c*]quinoline-1,1'-cyclopropan]-3-one (2o)

pale green solid, 71 mg, 86% yield; *dr* > 20:1; m. p. 180 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.18-7.12 (m, 3H), 7.03 (d, *J* = 2.0 Hz, 1H), 6.92 (d, *J* = 7.6 Hz, 1H), 6.77-6.75 (m, 2H), 3.74 (s, 3H), 3.32 (d, *J* = 10.8 Hz, 1H), 3.10 (s, 3H), 1.78 (d, *J* = 10.4 Hz, 1H), 1.59-1.53 (m, 1H), 1.46 (s,

3H), 0.80-0.75 (m, 1H), 0.43 (dt, J_1 = 6.4 Hz, J_2 = 10.0 Hz, 1H), 0.25 (dt, J_1 = 6.0 Hz, J_2 = 10.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 174.5, 157.3, 143.1, 134.9, 134.8, 128.0, 125.0, 124.3, 119.8, 119.2, 113.2, 55.1, 52.1, 42.9, 39.0, 30.9, 29.6, 25.3, 11.8, 6.1; IR (CH_2Cl_2): 2997, 2953, 1690, 1606, 1593, 1512, 1452, 1416, 1394, 1308, 1295, 1276, 1252, 1242, 1223, 1189, 1096, 1082, 1032, 1025, 1011, 976, 926, 842, 825, 806, 792, 747, 720, 700 cm^{-1}; HRMS (ESI) Calcd. For $C_{22}H_{23}BrNO_2$ $(M+H)^+$ requires: 412.0907, Found: 412.0904.

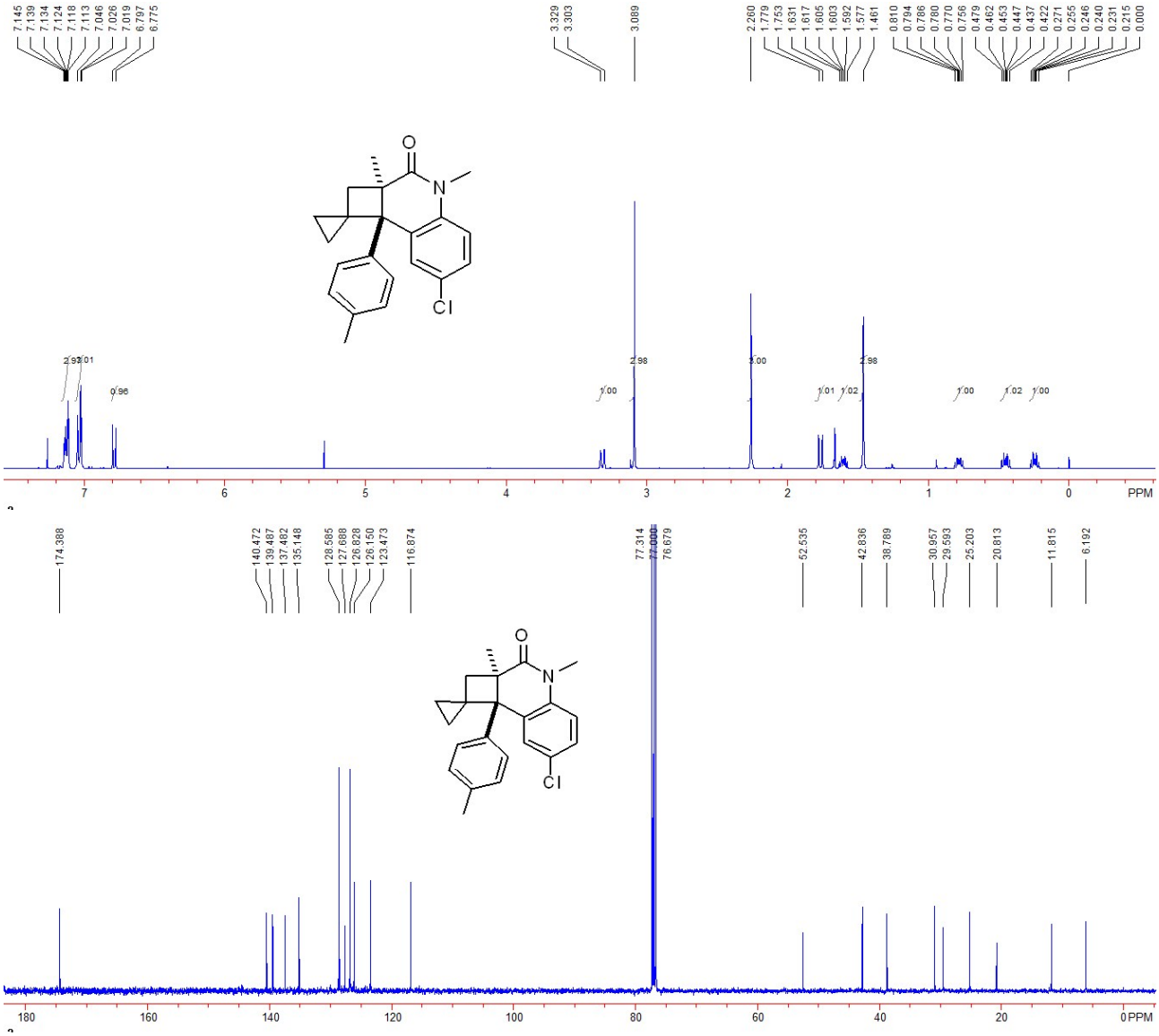


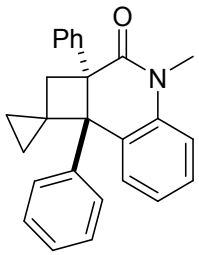




***anti*-7-Chloro-2a,4-dimethyl-8b-(p-tolyl)-2,2a,4,8b-tetrahydro-3*H*-spiro[cyclobuta[*c*]quinoline-1,1'-cyclopropan]-3-one (2p)**

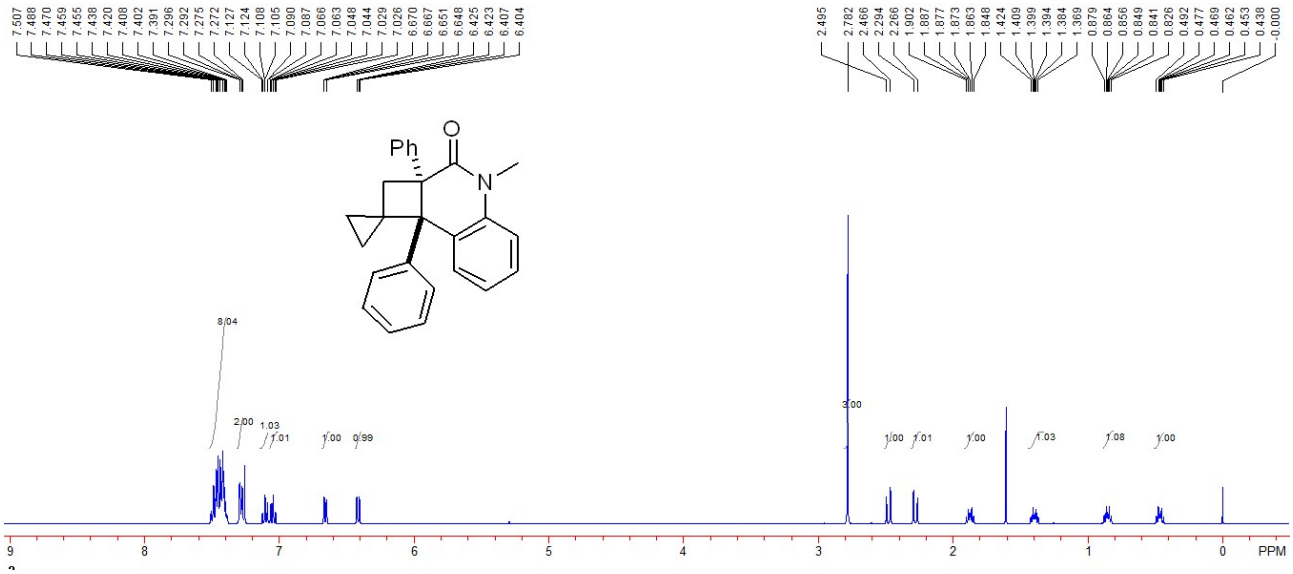
pale green solid, 58 mg, 83% yield; *dr* > 20:1; m. p. 185 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.15-7.11 (m, 3H), 7.05-7.02 (m, 3H), 6.79 (d, J = 8.8 Hz, 1H), 3.32 (d, J = 10.4 Hz, 1H), 3.09 (s, 3H), 2.26 (s, 3H), 1.77 (d, J = 10.4 Hz, 1H), 1.63-1.58 (m, 1H), 1.46 (s, 3H), 0.81-0.76 (m, 1H), 0.45 (dt, J_1 = 6.4 Hz, J_2 = 10.4 Hz, 1H), 0.24 (dt, J_1 = 6.0 Hz, J_2 = 10.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 174.4, 140.5, 139.5, 137.5, 135.1, 128.6, 127.7, 126.8, 126.2, 123.5, 116.9, 52.5, 42.8, 38.8, 31.0, 29.6, 25.2, 20.8, 11.8, 6.2; IR (CH_2Cl_2): 2980, 1684, 1513, 1465, 1447, 1415, 1314, 1248, 1224, 1104, 1012, 944, 824, 816, 752, 738 cm^{-1}; HRMS (ESI) Calcd. For $C_{22}H_{23}ClNO$ $(M+H)^+$ requires: 352.1463, Found: 352.1459.

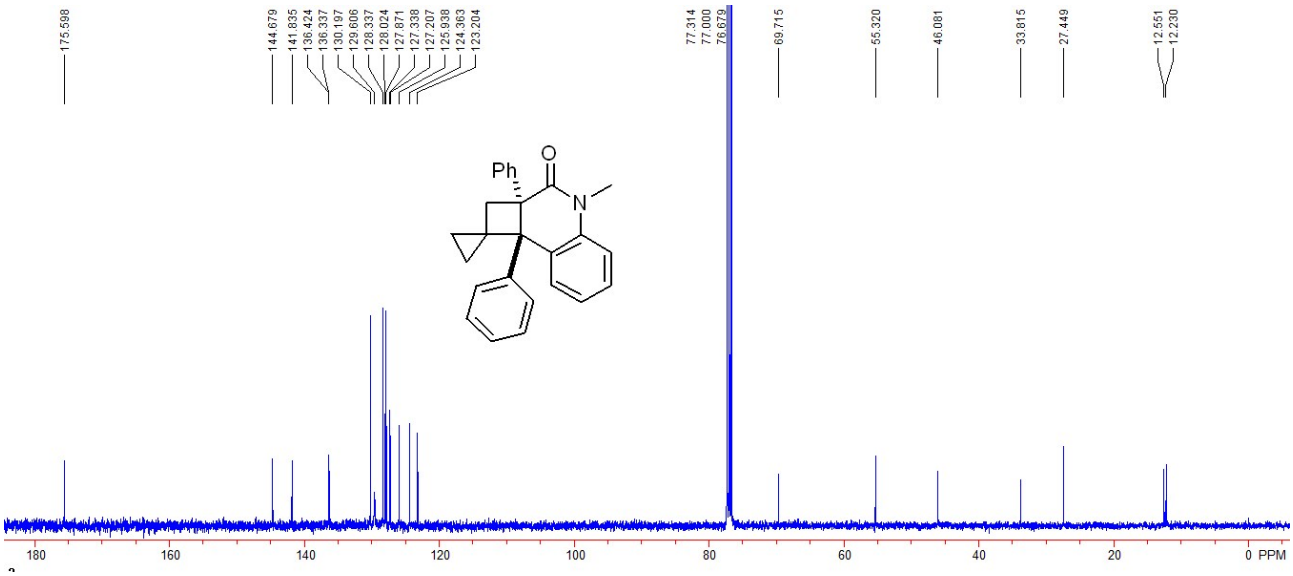


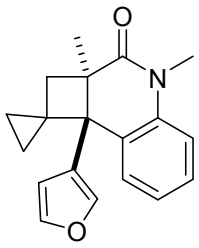


***anti*-4-Methyl-2a,8b-diphenyl-2,2a,4,8b-tetrahydro-3*H*-spiro[cyclobuta[*c*]quinoline-1,1'-cyclopropan]-3-one (2q)**

pale green solid, 68 mg, 91% yield; *dr* > 20:1; m. p. 195 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.51-7.40 (m, 8H), 7.30-7.27 (m, 2H), 7.11 (td, J_1 = 1.2 Hz, J_2 = 7.6 Hz, 1H), 7.05 (td, J_2 = 7.6 Hz, J_1 = 1.2 Hz, 1H), 6.66 (dd, J_1 = 1.2 Hz, J_2 = 7.6 Hz, 1H), 6.43-6.40 (m, 1H), 2.78 (s, 3H), 2.48 (d, J = 11.6 Hz, 1H), 2.28 (d, J = 11.2 Hz, 1H), 1.90-1.85 (m, 1H), 1.42-1.37 (m, 1H), 0.85 (dt, J_1 = 6.0 Hz, J_2 = 10.0 Hz, 1H), 0.47 (dt, J_1 = 6.0 Hz, J_2 = 10.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 175.6, 144.7, 141.8, 136.4, 136.3, 130.2, 129.6, 128.3, 128.0, 127.9, 127.3, 127.2, 125.9, 124.4, 123.2, 55.3, 46.1, 33.8, 27.4, 12.6, 12.2; IR (CH_2Cl_2): 2988, 2934, 1666, 1598, 1497, 1453, 1442, 1369, 1040, 1003, 984, 783, 761, 740, 713, 693, 668 cm^{-1}; HRMS (ESI) Calcd. For $C_{26}H_{24}NO$ $(M+H)^+$ requires: 366.1852, Found: 366.1845.

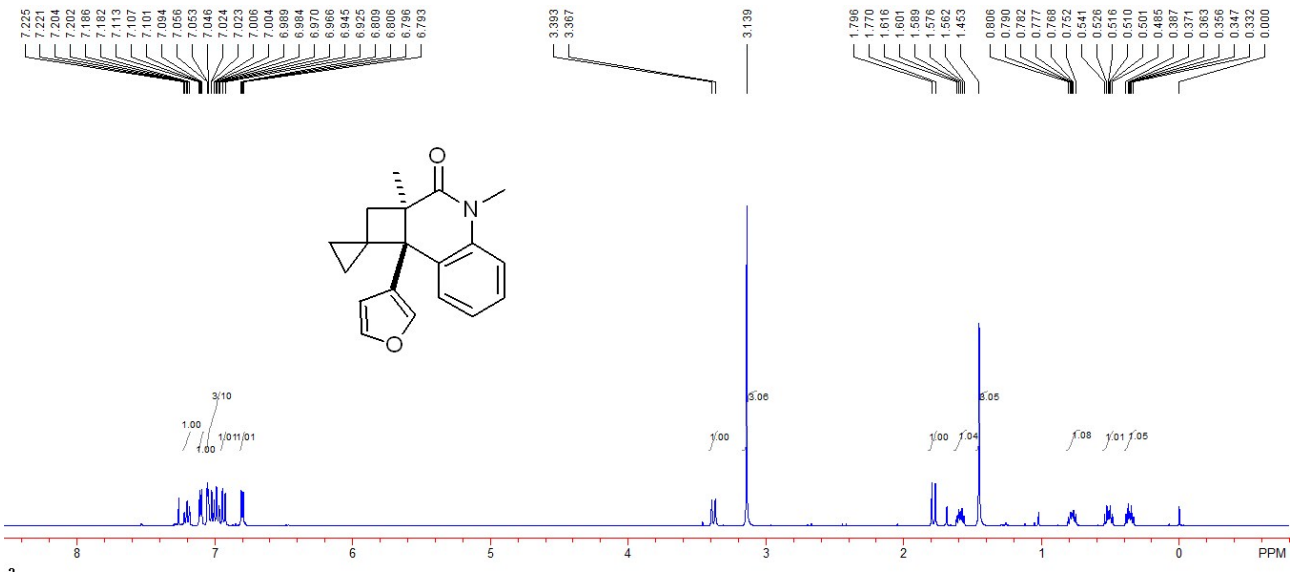


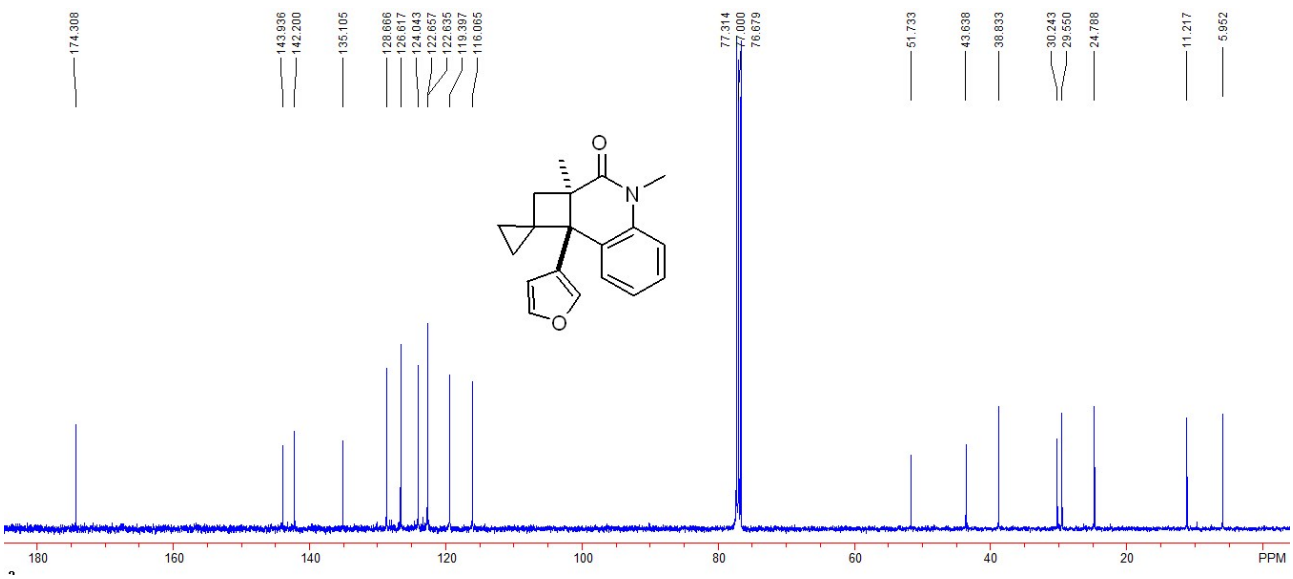


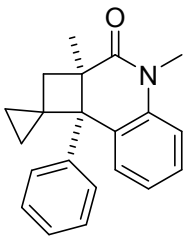


***anti*-8b-(furan-3-yl)-2a,4-Dimethyl-2,2a,4,8b-tetrahydro-3*H*-spiro[cyclobuta[*c*]quinoline-1,1'-cyclopropan]-3-one (2r)**

pale green solid, 50 mg, 75% yield; *dr* > 20:1; m. p. 180 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.23-7.18 (m, 1H), 7.11-7.09 (m, 1H), 7.06-6.97 (m, 3H), 6.94 (d, J = 8.0 Hz, 1H), 6.80 (dd, J_1 = 1.2 Hz, J_2 = 5.2 Hz, 1H), 3.38 (d, J = 10.4 Hz, 1H), 3.14 (s, 3H), 1.78 (d, J = 10.4 Hz, 1H), 1.62-1.56 (m, 1H), 1.45 (s, 3H), 0.81-0.75 (m, 1H), 0.51 (dt, J_1 = 6.0 Hz, J_2 = 10.0 Hz, 1H), 0.36 (dt, J_1 = 6.0 Hz, J_2 = 10.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 174.3, 143.9, 142.2, 135.1, 128.7, 126.6, 124.0, 122.7, 122.6, 119.4, 116.1, 51.7, 43.6, 38.8, 30.2, 29.6, 24.8, 11.2, 6.0; IR (CH_2Cl_2): 2995, 2930, 1679, 1450, 1416, 1319, 1256, 1230, 1095, 1079, 1043, 794, 781, 750, 669, 659 cm^{-1}; HRMS (ESI) Calcd. For $C_{19}H_{19}NO_2$ $(M+H)^+$ requires: 294.1489, Found: 294.1484.



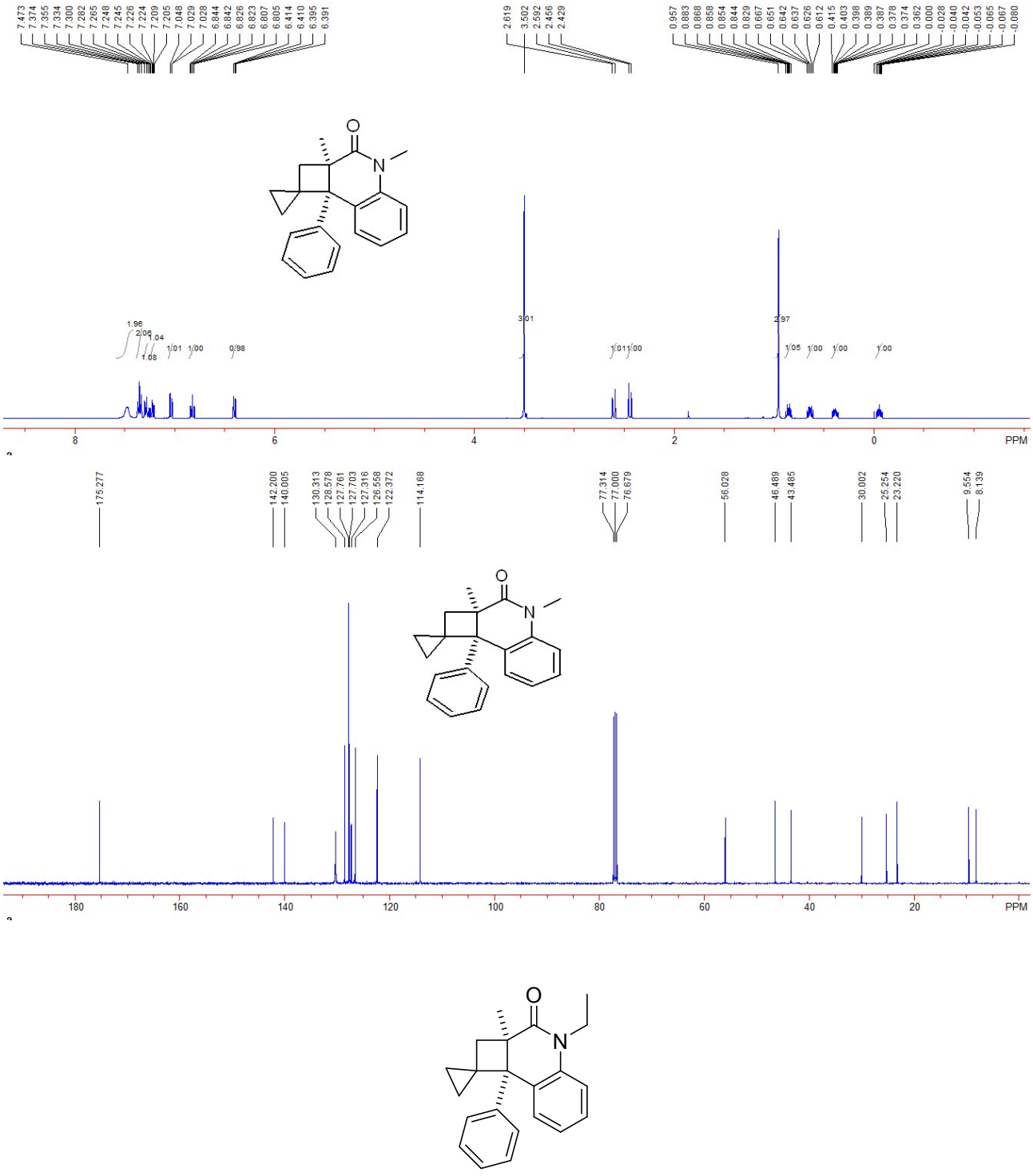




syn-2a,4-Dimethyl-8b-phenyl-2,2a,4,8b-tetrahydro-3*H*-spiro[cyclobuta[*c*]quinoline-1,1'-cyclopropan]-3-one (3a)

pale green solid, 55 mg, 91% yield; *dr* > 20:1; m. p. 169 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.47 (s, 2H), 7.37-7.33 (m, 2H), 7.30-7.26 (m, 1H), 7.25-7.21 (m, 1H), 7.05-7.03 (m, 1H), 6.82 (td, J_2 = 7.2 Hz, J_1 = 0.8 Hz, 1H), 6.40 (dd, J_2 = 7.6 Hz, J_1 = 1.6 Hz, 1H), 3.50 (s, 3H), 2.61 (d, J = 10.8 Hz, 1H), 2.44 (d, J = 10.8 Hz, 1H), 0.96 (s, 3H), 0.86 (dt, J_1 = 6.0 Hz, J_2 = 10.0 Hz, 1H), 0.67-0.61 (m, 1H), 0.42-0.36 (m, 1H), -0.03--0.08 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 175.3, 142.2,

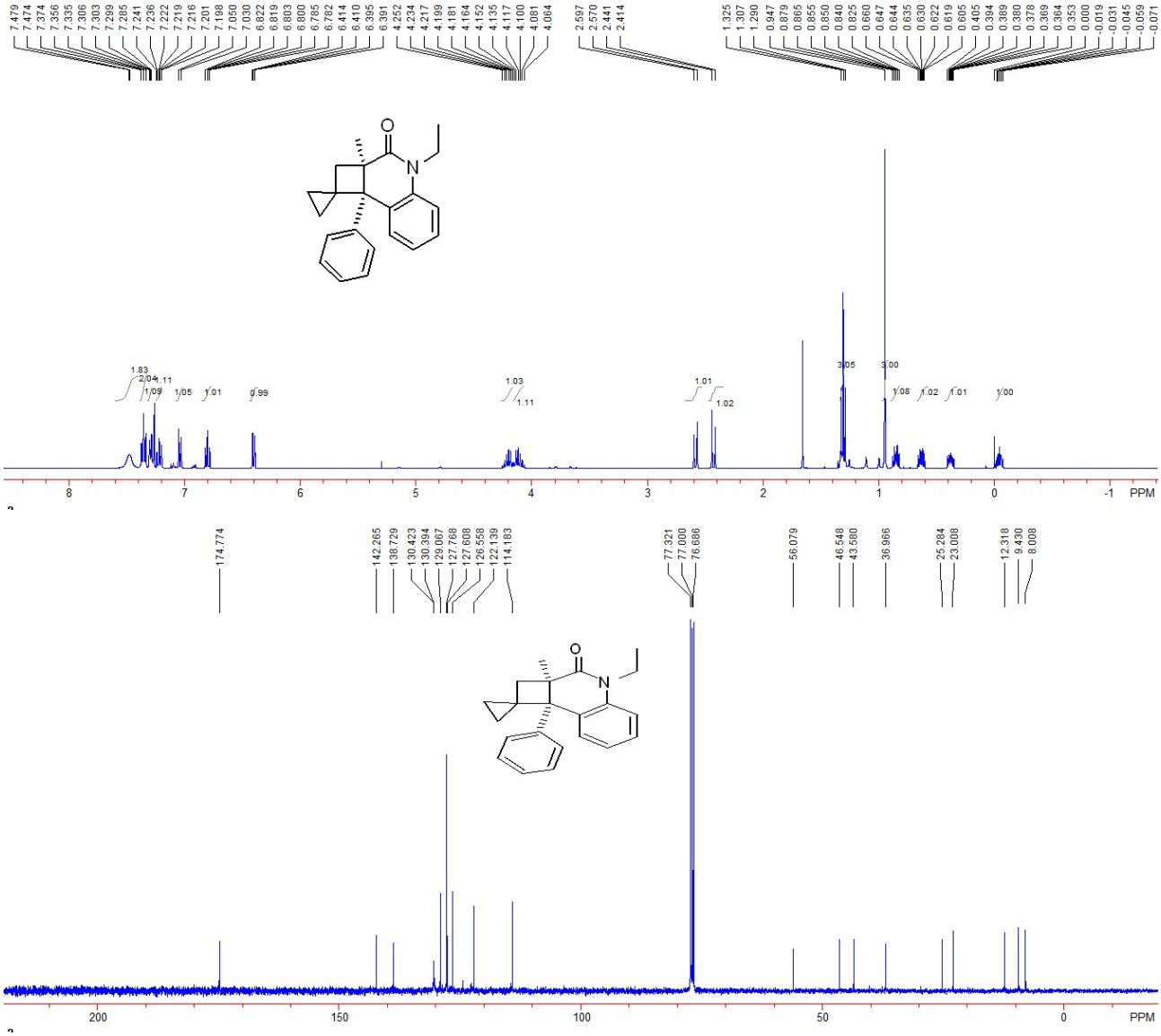
140.0, 130.3, 128.6, 127.8, 127.7, 127.3, 126.6, 122.4, 114.2, 56.0, 46.5, 43.5, 30.0, 25.3, 23.2, 9.6, 8.1; IR (CH_2Cl_2): 2917, 2849, 1652, 1595, 1510, 1495, 1452, 1379, 1363, 1351, 1305, 1276, 1100, 1054, 1012, 962, 920, 816, 760, 749, 718, 704, 669 cm^{-1}; HRMS (ESI) Calcd. For $C_{21}H_{22}NO$ $(M+H)^+$ requires: 304.1696, Found: 304.1691.

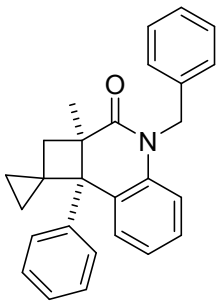


syn-4-Ethyl-2a-methyl-8b-phenyl-2,2a,4,8b-tetrahydro-3*H*-spiro[cyclobuta[*c*]quinoline-1,1'-cyclopropan]-3-one (3b)

pale green solid, 56 mg, 89% yield; *dr* > 20:1; m. p. 198 °C; ^1H NMR (400 MHz, $CDCl_3$, TMS) δ

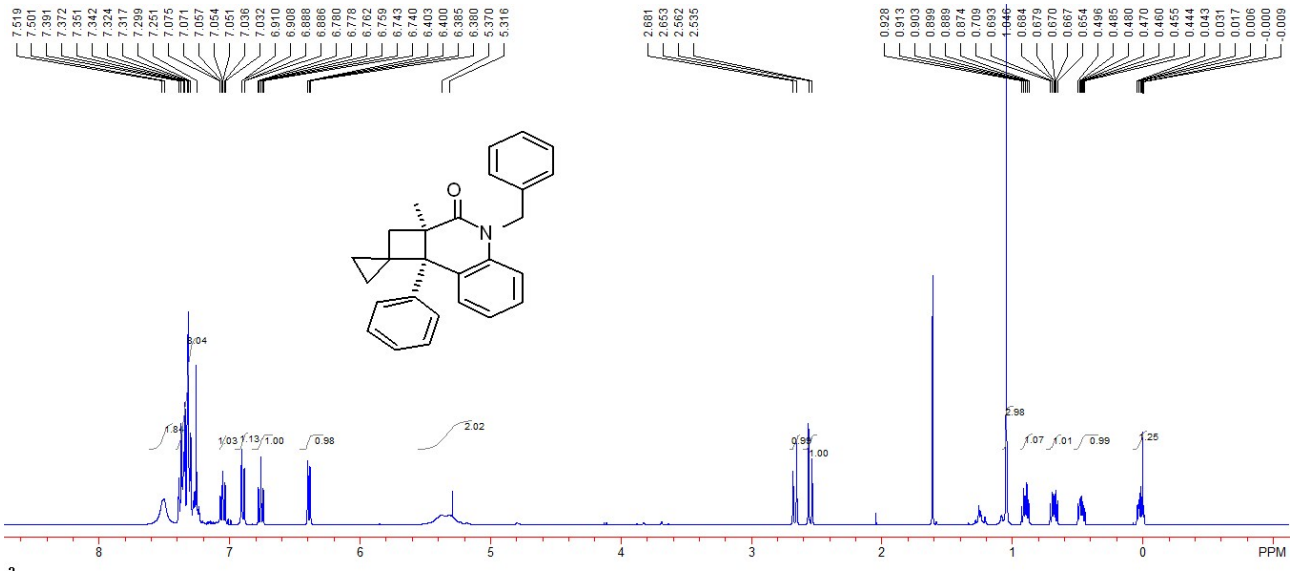
7.48 (s, 2H), 7.37-7.34 (m, 2H), 7.31-7.29 (m, 1H), 7.24-7.20 (m, 1H), 7.04 (d, J = 8.0 Hz, 1H), 6.80 (td, J_2 = 7.6 Hz, J_1 = 1.2 Hz, 1H), 6.40 (dd, J_2 = 7.6 Hz, J_1 = 1.6 Hz, 1H), 4.25-4.15 (m, 1H), 4.14-4.06 (m, 1H), 2.58 (d, J = 10.8 Hz, 1H), 2.43 (d, J = 10.8 Hz, 1H), 1.31 (t, J = 7.2 Hz, 3H), 0.95 (s, 3H), 0.85 (dt, J_1 = 6.0 Hz, J_2 = 10.0 Hz, 1H), 0.66-0.61 (m, 1H), 0.41-0.35 (m, 1H), -0.02--0.07 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 174.8, 142.3, 138.7, 130.42, 130.39, 129.1, 127.8, 127.6, 126.6, 122.1, 114.2, 56.1, 46.5, 43.6, 37.0, 25.3, 23.0, 12.3, 9.4, 8.0; IR (CH_2Cl_2): 2988, 2967, 1671, 1456, 1372, 1355, 1337, 1297, 1246, 1215, 1194, 1102, 1083, 1044, 1019, 763, 746, 718, 707, 659 cm^{-1}; HRMS (ESI) Calcd. For $C_{22}H_{24}NO$ $(M+H)^+$ requires: 318.1852, Found: 318.1846.

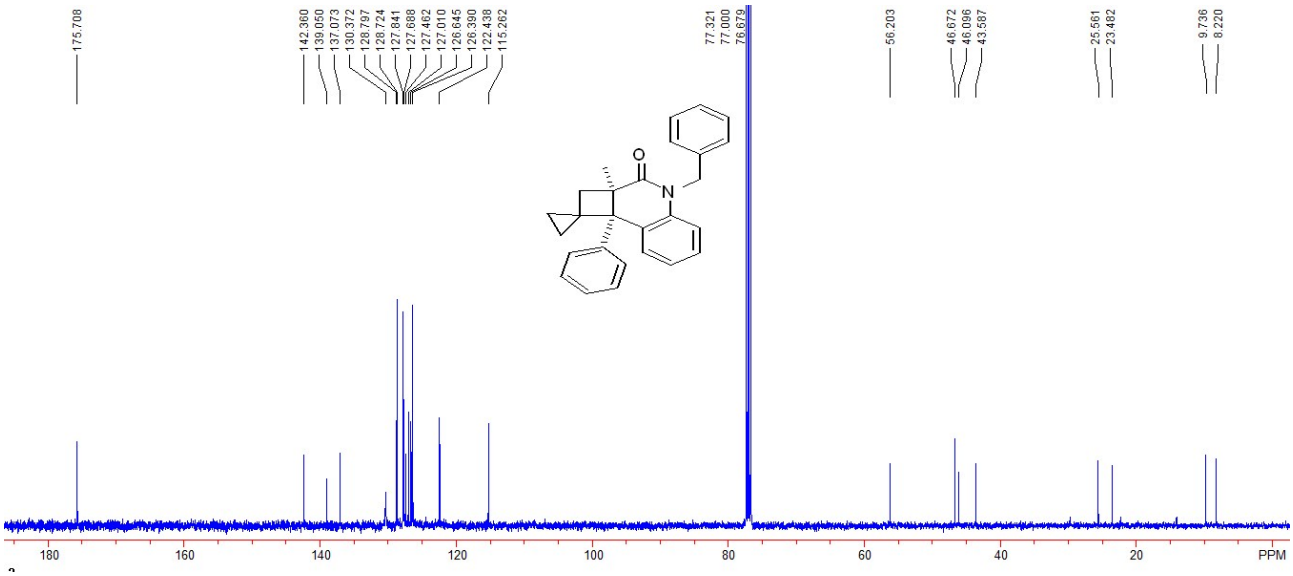


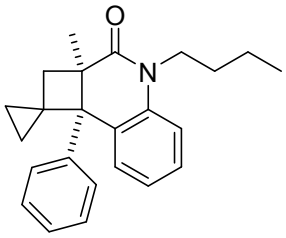


syn-4-Benzyl-2a-methyl-8b-phenyl-2,2a,4,8b-tetrahydro-3*H*-spiro[cyclobuta[*c*]quinoline-1,1'-cyclopropan]-3-one (3c)

pale green solid, 72 mg, 95% yield; *dr* > 20:1; m. p. 198 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.52-7.50 (m, 2H), 7.39-7.25 (m, 8H), 7.08-7.03 (m, 1H), 6.90 (dd, J_2 = 8.8 Hz, J_1 = 0.8 Hz, 1H), 6.76 (td, J_2 = 7.2 Hz, J_1 = 0.8 Hz, 1H), 6.39 (dd, J_2 = 7.2 Hz, J_1 = 1.2 Hz, 1H), 5.37-5.32 (m, 2H), 2.67 (d, J = 11.2 Hz, 1H), 2.55 (d, J = 10.8 Hz, 1H), 1.05 (s, 3H), 0.90 (dt, J_1 = 6.0 Hz, J_2 = 10.0 Hz, 1H), 0.71-0.65 (m, 1H), 0.50-0.44 (m, 1H), 0.04--0.01 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 175.7, 142.4, 139.1, 137.1, 130.4, 128.8, 128.7, 127.8, 127.7, 127.5, 127.0, 126.6, 126.4, 122.4, 115.3, 56.2, 46.7, 46.1, 43.6, 25.6, 23.5, 9.7, 8.2; IR (CH_2Cl_2): 2987, 1692, 1599, 1576, 1494, 1480, 1450, 1435, 1352, 1339, 1308, 1239, 1164, 1109, 1078, 1027, 1101, 955, 919, 895, 769, 757, 729, 716, 707, 694, 680, 656 cm^{-1}; HRMS (ESI) Calcd. For $C_{27}H_{26}NO$ $(M+H)^+$ requires: 380.2009, Found: 380.2003.

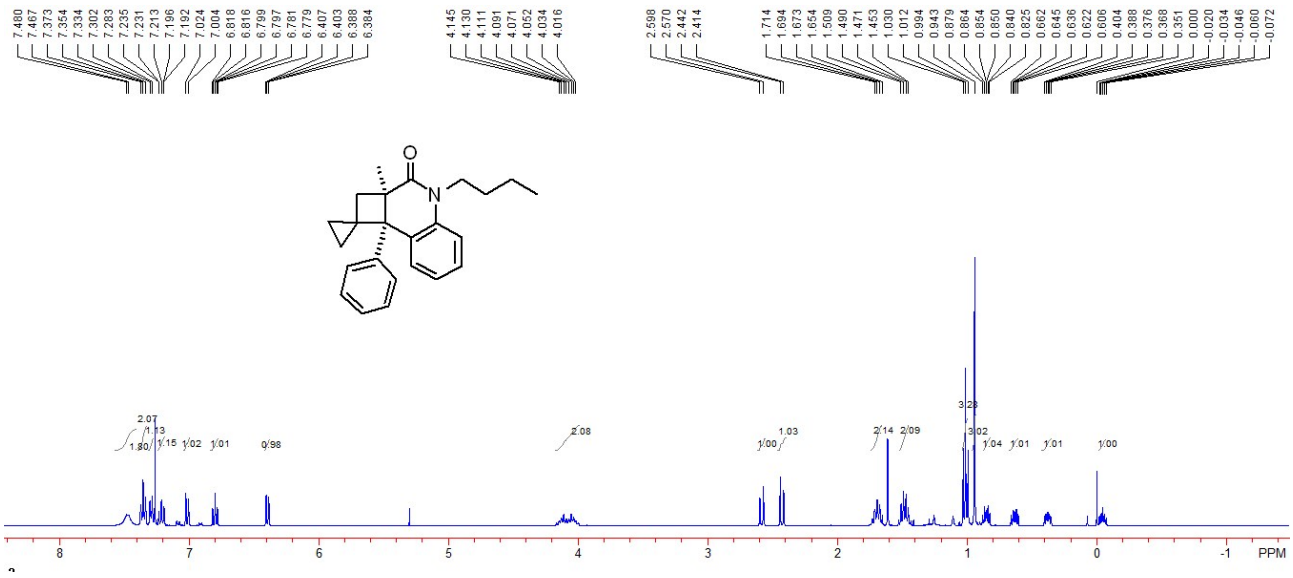


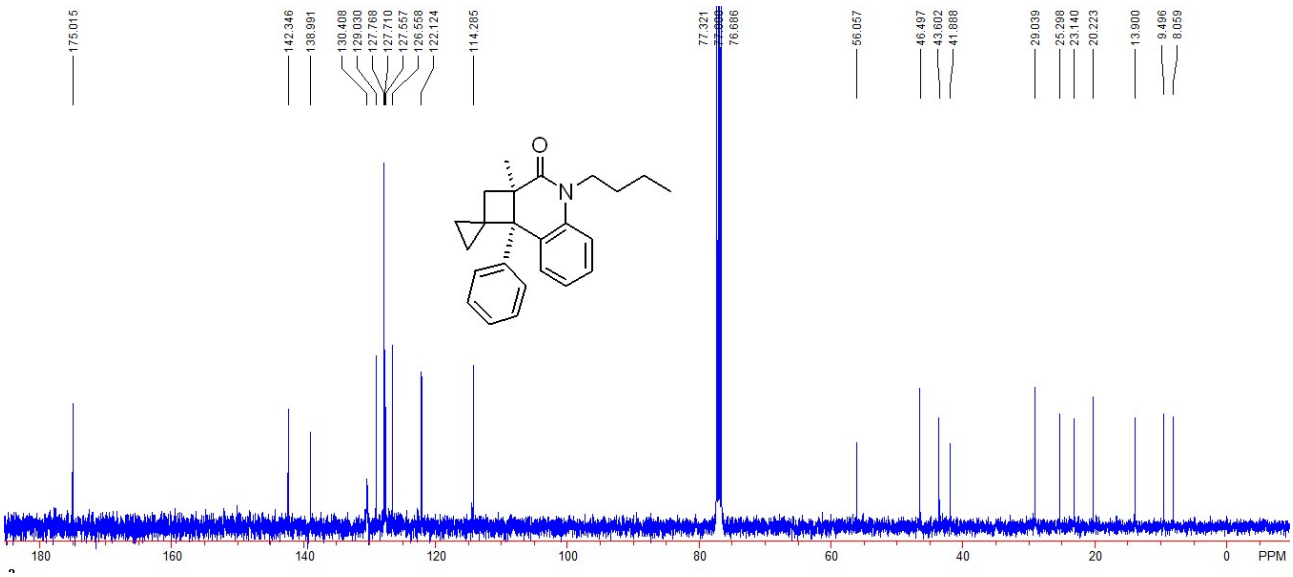


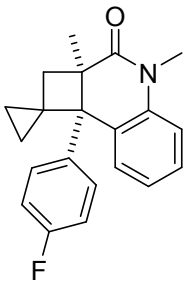


syn-4-Butyl-2a-methyl-8b-phenyl-2,2a,4,8b-tetrahydro-3*H*-spiro[cyclobuta[*c*]quinoline-1,1'-cyclopropan]-3-one (3d)

pale green solid, 66 mg, 95% yield; *dr* > 20:1; m. p. 179 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.48-7.47 (m, 2H), 7.37-7.33 (m, 2H), 7.30-7.28 (m, 1H), 7.24-7.19 (m, 1H), 7.01 (d, J = 8.0 Hz, 1H), 6.80 (td, J_2 = 7.6 Hz, J_1 = 0.8 Hz, 1H), 6.40 (dd, J_2 = 7.6 Hz, J_1 = 1.2 Hz, 1H), 4.15-4.02 (m, 2H), 2.58 (d, J = 11.2 Hz, 1H), 2.43 (d, J = 11.2 Hz, 1H), 1.71-1.65 (m, 1H), 1.51-1.45 (m, 1H), 1.01 (t, J = 7.2 Hz, 3H), 0.94 (s, 3H), 0.88-0.83 (m, 1H), 0.66-0.61 (m, 1H), 0.40-0.35 (m, 1H), -0.02--0.07 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 175.0, 142.3, 139.0, 130.4, 129.0, 127.8, 127.7, 127.6, 126.6, 122.1, 114.3, 56.1, 46.5, 43.6, 41.9, 29.0, 25.3, 23.1, 20.2, 13.9, 9.5, 8.1; IR (CH_2Cl_2): 2937, 2920, 1648, 1590, 1510, 1480, 1442, 1369, 1353, 1311, 1266, 1009, 1002, 898, 836, 778, 759, 704, 689 cm^{-1}; HRMS (ESI) Calcd. For $C_{24}H_{28}NO$ $(M+H)^+$ requires: 346.2165, Found: 346.2159.



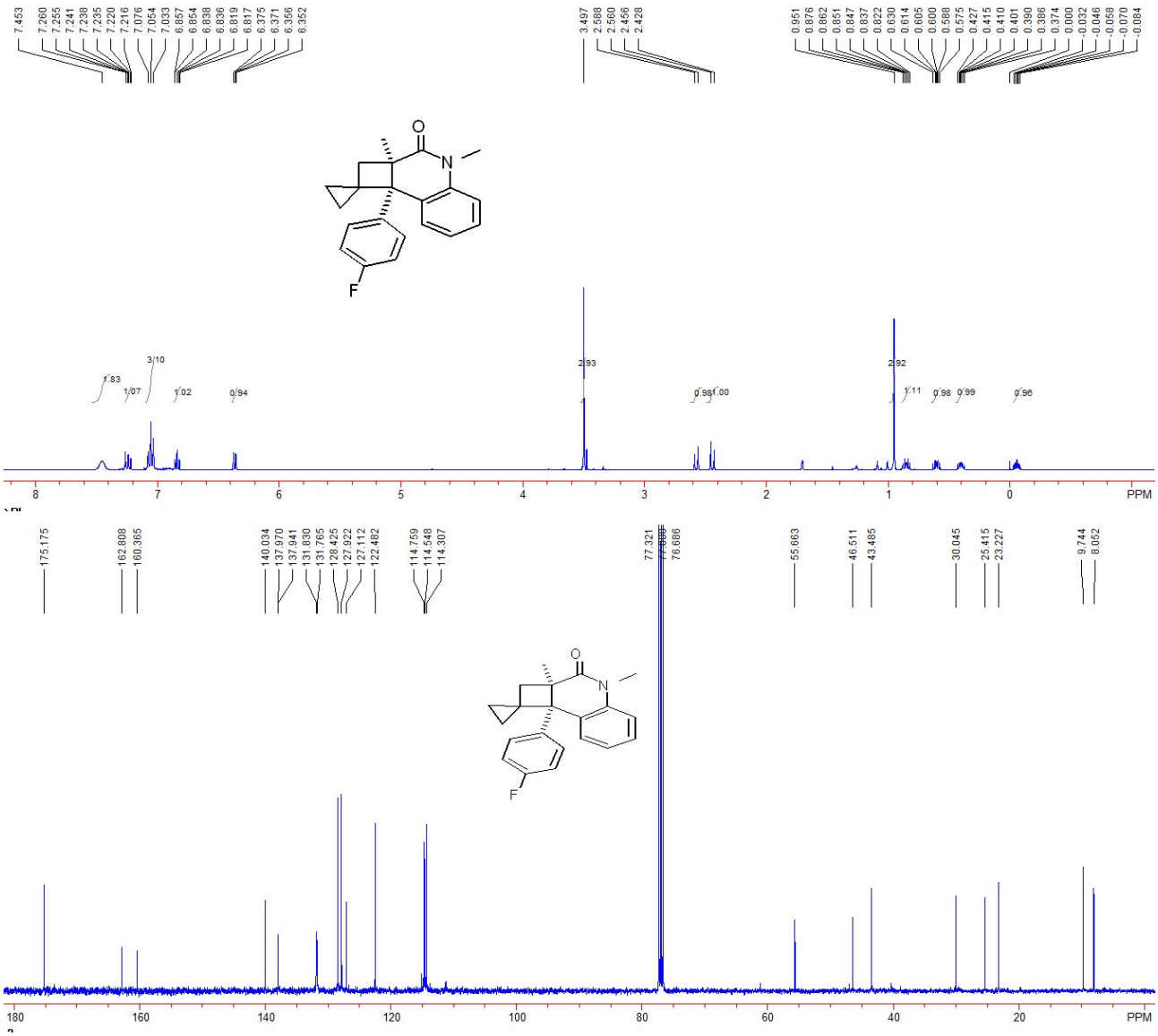


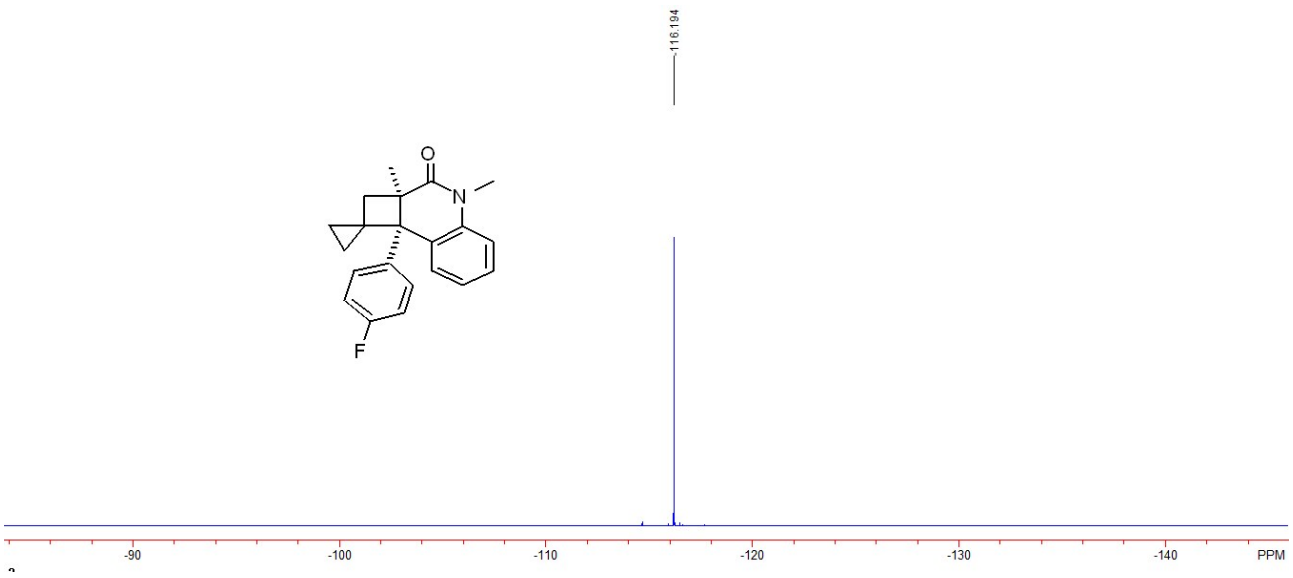


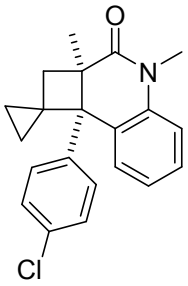
syn-8b-(4-fluorophenyl)-2a,4-Dimethyl-2,2a,4,8b-tetrahydro-3*H*-spiro[cyclobuta[*c*]quinoline-1,1'-cyclopropan]-3-one (3e)

pale green solid, 50 mg, 78% yield; *dr* > 20:1; m. p. 187 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.45 (s, 2H), 7.26-7.22 (m, 1H), 7.08-7.03 (m, 3H), 6.84 (td, J_2 = 7.6 Hz, J_1 = 1.2 Hz, 1H), 6.36 (dd, J_2 = 7.6 Hz, J_1 = 1.6 Hz, 1H), 3.50 (s, 3H), 2.57 (d, J = 11.2 Hz, 1H), 2.44 (d, J = 11.2 Hz, 1H), 0.95 (s, 3H), 0.85 (dt, J_1 = 6.0 Hz, J_2 = 10.0 Hz, 1H), 0.60 (dt, J_1 = 6.4 Hz, J_2 = 10.0 Hz, 1H), 0.43-

0.37 (m, 1H), -0.03--0.08 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 175.2, 161.6 (d, J = 244.3 Hz), 140.0, 138.0 (d, J = 2.9 Hz), 131.8 (d, J = 6.5 Hz), 128.4, 127.9, 127.1, 122.5, 114.7 (d, J = 21.1 Hz), 114.3, 55.7, 46.5, 43.5, 30.0, 25.4, 23.2, 9.7, 8.1; ^{19}F NMR (376 MHz, $CDCl_3$): δ -116.2; IR (CH_2Cl_2): 2966, 1645, 1596, 1506, 1478, 1496, 1451, 1364, 1354, 1306, 1281, 1221, 1131, 1110, 1091, 1014, 838, 824, 812, 749, 718, 707, 652 cm^{-1}; HRMS (ESI) Calcd. For $C_{21}H_{21}FNO$ $(M+H)^+$ requires: 322.1602, Found: 322.1596.

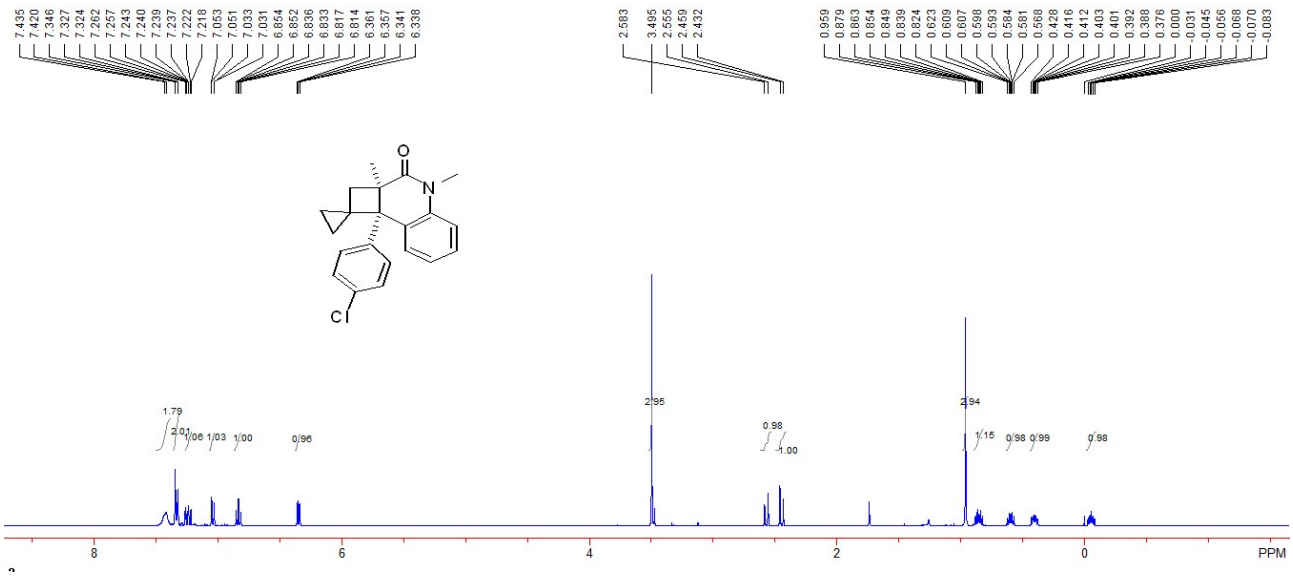


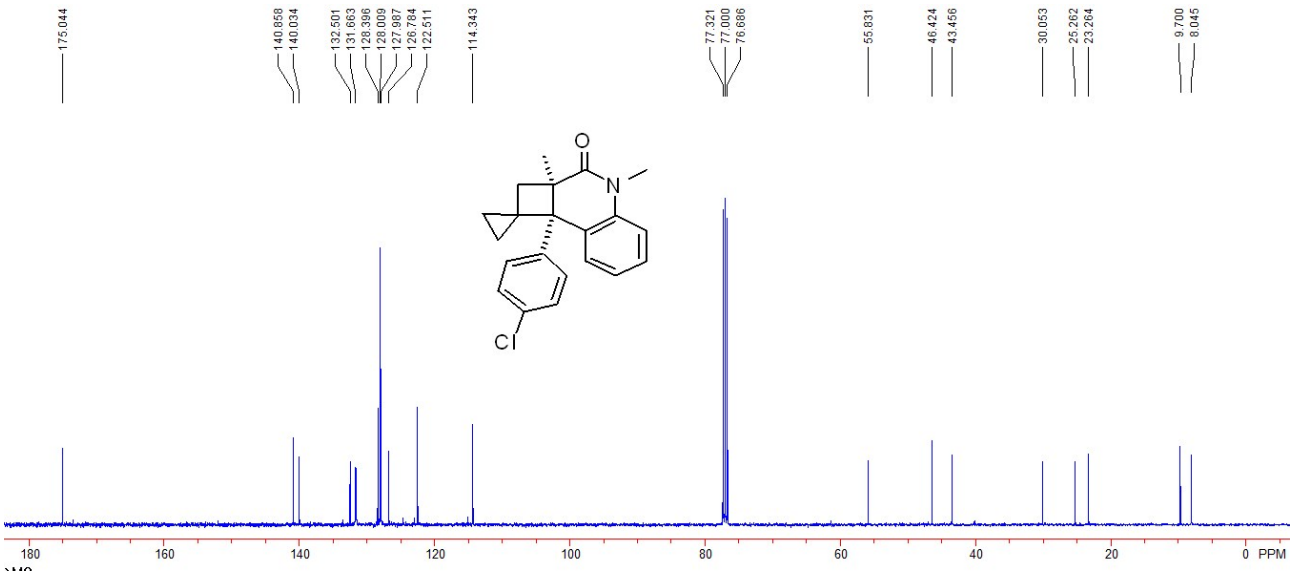


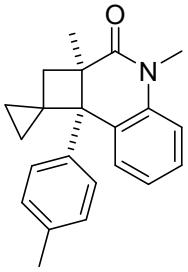


syn-8b-(4-chlorophenyl)-2a,4-Dimethyl-2,2a,4,8b-tetrahydro-3*H*-spiro[cyclobuta[*c*]quinoline-1,1'-cyclopropan]-3-one (3f)

pale green solid, 54 mg, 80% yield; *dr* > 20:1; m. p. 187 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.43-7.42 (m, 2H), 7.34-7.32 (m, 2H), 7.26-7.22 (m, 1H), 7.04 (dd, J_2 = 8.0 Hz, J_1 = 0.8 Hz, 1H), 6.83 (td, J_2 = 7.6 Hz, J_1 = 1.2 Hz, 1H), 6.35 (dd, J_2 = 8.0 Hz, J_1 = 1.2 Hz, 1H), 3.50 (s, 3H), 2.57 (d, J = 11.2 Hz, 1H), 2.45 (d, J = 10.8 Hz, 1H), 0.96 (s, 3H), 0.88-0.82 (m, 1H), 0.62-0.57 (m, 1H), 0.43-0.37 (m, 1H), -0.03--0.08 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 175.0, 140.9, 140.0, 132.5, 131.7, 128.4, 128.01, 127.99, 126.8, 122.5, 114.3, 55.8, 46.4, 43.5, 30.1, 25.3, 23.3, 9.7, 8.0; IR (CH_2Cl_2): 2972, 2927, 1648, 1595, 1495, 1453, 1370, 1354, 1306, 1278, 1119, 1090, 1056, 1024, 827, 812, 754, 702, 669 cm^{-1}; HRMS (ESI) Calcd. For $C_{21}H_{21}ClNO$ $(M+H)^+$ requires: 338.1306, Found: 338.1300.



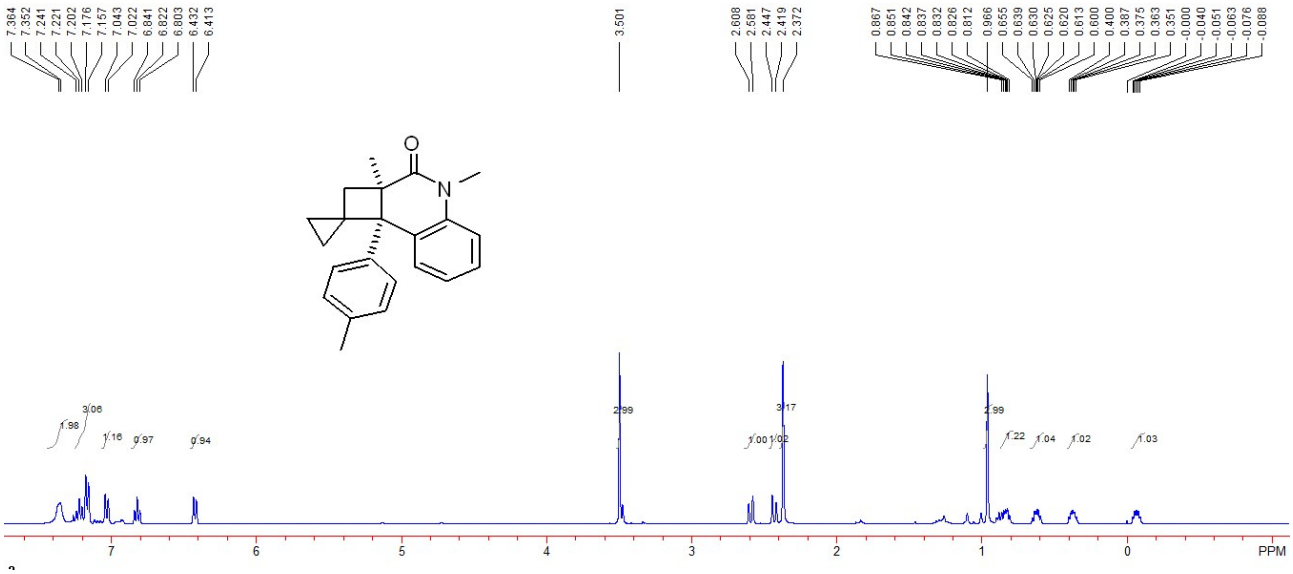


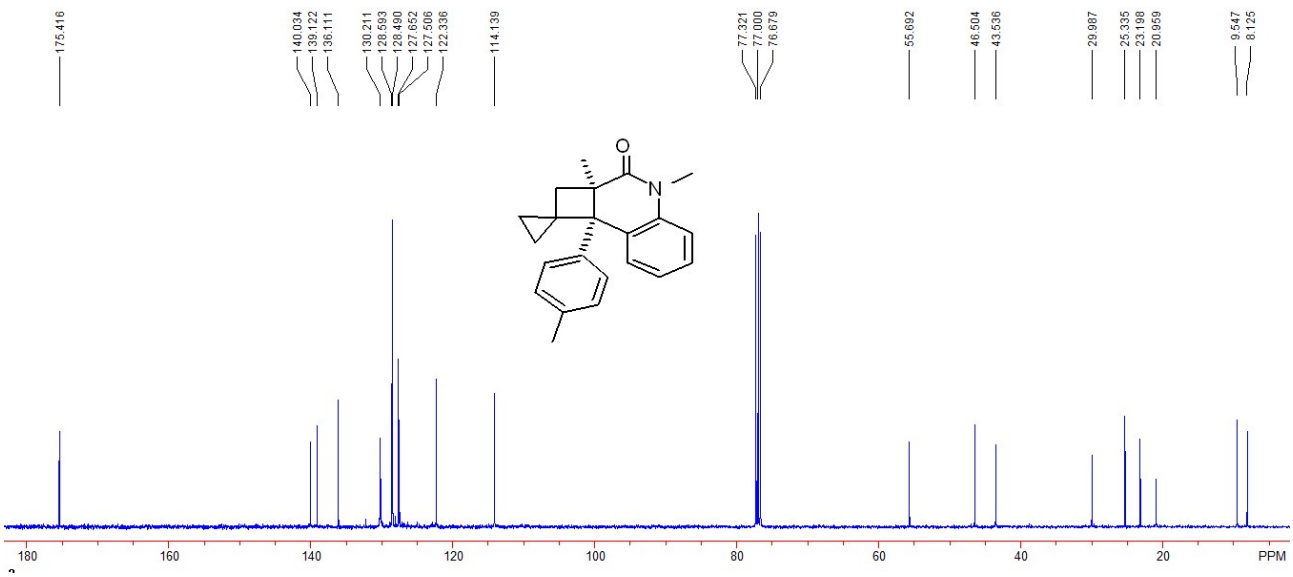


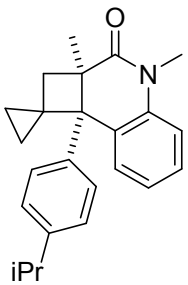
syn-2a,4-Dimethyl-8b-(p-tolyl)-2,2a,4,8b-tetrahydro-3*H*-spiro[cyclobuta[*c*]quinoline-1,1'-cyclopropan]-3-one (3g)

pale green solid, 53 mg, 84% yield; *dr* > 20:1; m. p. 190 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.36-7.35 (m, 2H), 7.24-7.16 (m, 3H), 7.03 (d, *J* = 8.4 Hz, 1H), 6.82 (t, *J* = 7.6 Hz, 1H), 6.42 (d, *J* = 7.6 Hz, 1H), 3.50 (s, 3H), 2.59 (d, *J* = 10.8 Hz, 1H), 2.43 (d, *J* = 11.2 Hz, 1H), 2.37 (s, 3H), 0.97 (s, 3H), 0.87-0.81 (m, 1H), 0.66-0.60 (m, 1H), 0.40-0.35 (m, 1H), -0.04--0.09 (m, 1H); ^{13}C NMR (100

MHz, $CDCl_3$, TMS) δ 175.4, 140.0, 139.1, 136.1, 130.2, 128.6, 128.5, 127.7, 127.5, 122.3, 114.1, 55.7, 46.5, 43.5, 30.0, 25.3, 23.2, 21.0, 9.5, 8.1; IR (CH_2Cl_2): 2960, 2929, 1654, 1596, 1467, 1448, 1365, 1352, 1281, 1213, 1108, 1086, 1057, 938, 877, 825, 750, 728 cm^{-1}; HRMS (ESI) Calcd. For $C_{22}H_{24}NO$ $(M+H)^+$ requires: 318.1852, Found: 318.1846.

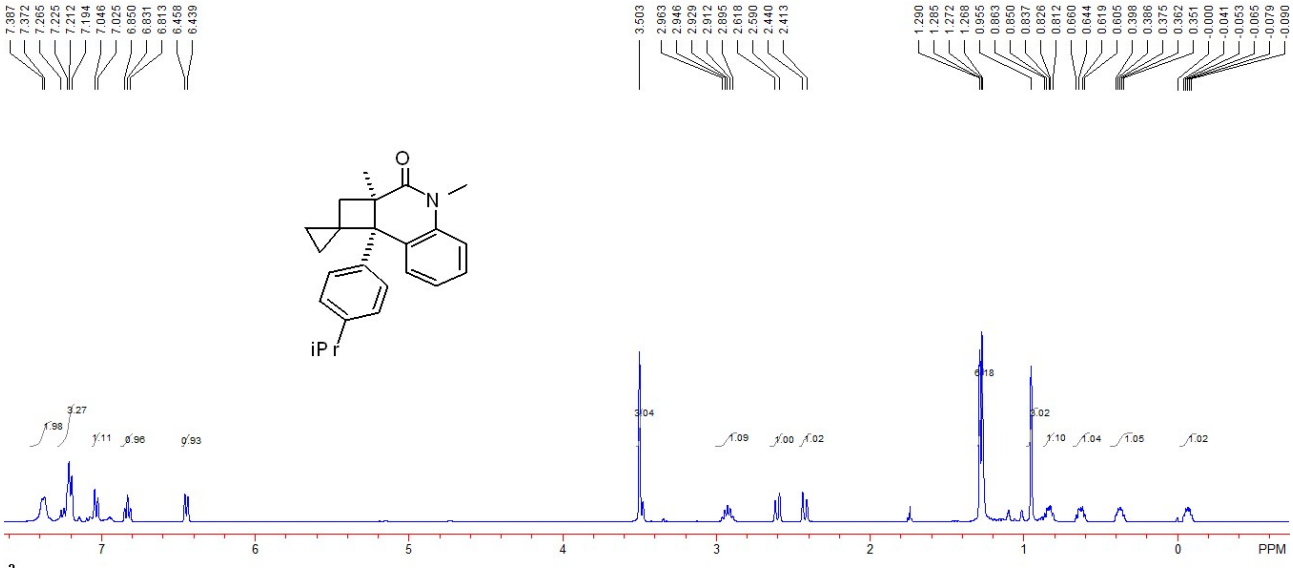


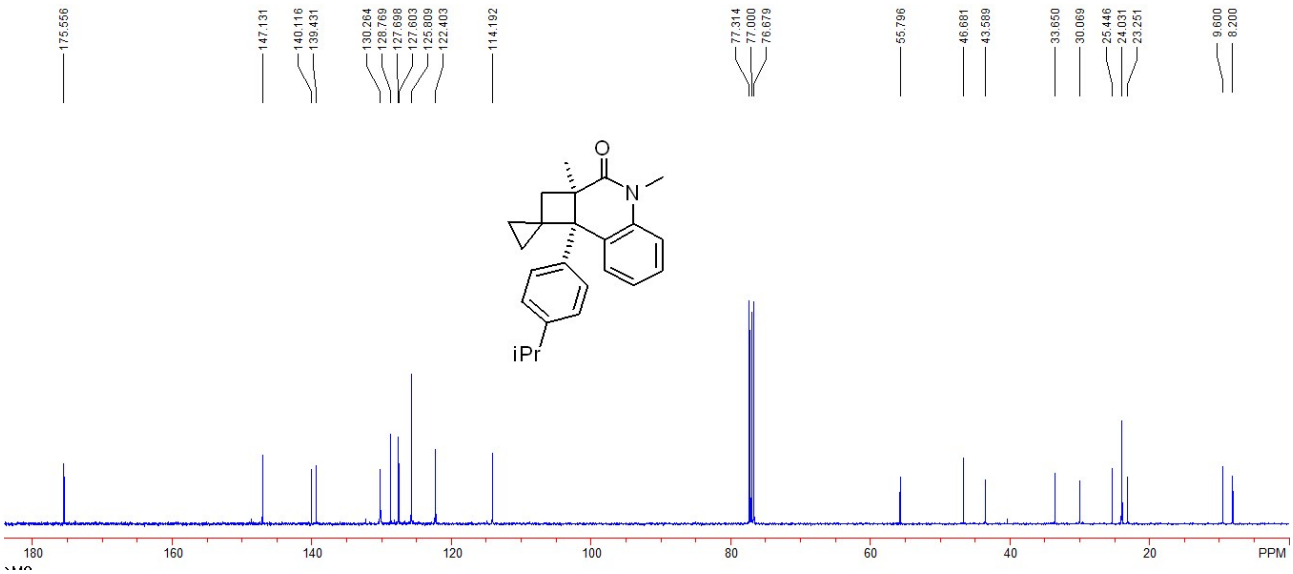


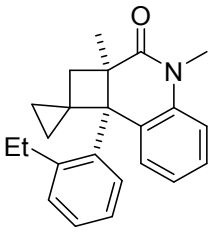


***syn*-8b-(4-isopropylphenyl)-2a,4-Dimethyl-2,2a,4,8b-tetrahydro-3*H*-spiro[cyclobuta[*c*]quinoline-1,1'-cyclopropan]-3-one (3h)**

pale green solid, 62 mg, 89% yield; *dr* > 20:1; m. p. 190 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.38 (br, 2H), 7.26-7.19 (m, 3H), 7.04 (d, *J* = 8.4 Hz, 1H), 6.83 (t, *J* = 7.6 Hz, 1H), 6.45 (d, *J* = 7.6 Hz, 1H), 3.50 (s, 3H), 2.96-2.90 (m, 1H), 2.60 (d, *J* = 11.2 Hz, 1H), 2.43 (d, *J* = 10.8 Hz, 1H), 1.28 (dd, J_2 = 7.2 Hz, J_1 = 2.0 Hz, 6H), 0.96 (s, 3H), 0.86-0.81 (m, 1H), 0.66-0.61 (m, 1H), 0.40-0.35 (m, 1H), -0.04--0.09 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 175.6, 147.1, 140.1, 139.4, 130.3, 128.8, 127.7, 127.6, 125.8, 122.4, 114.2, 55.8, 46.7, 43.6, 33.7, 30.1, 25.4, 24.0, 23.3, 9.6, 8.2; IR (CH_2Cl_2): 2958, 2931, 1649, 1596, 1469, 1452, 1358, 1308, 1283, 1109, 1092, 1060, 878, 830, 758, 750, 667, 652 cm^{-1}; HRMS (ESI) Calcd. For $C_{24}H_{28}NO$ $(M+H)^+$ requires: 346.2165, Found: 346.2160.

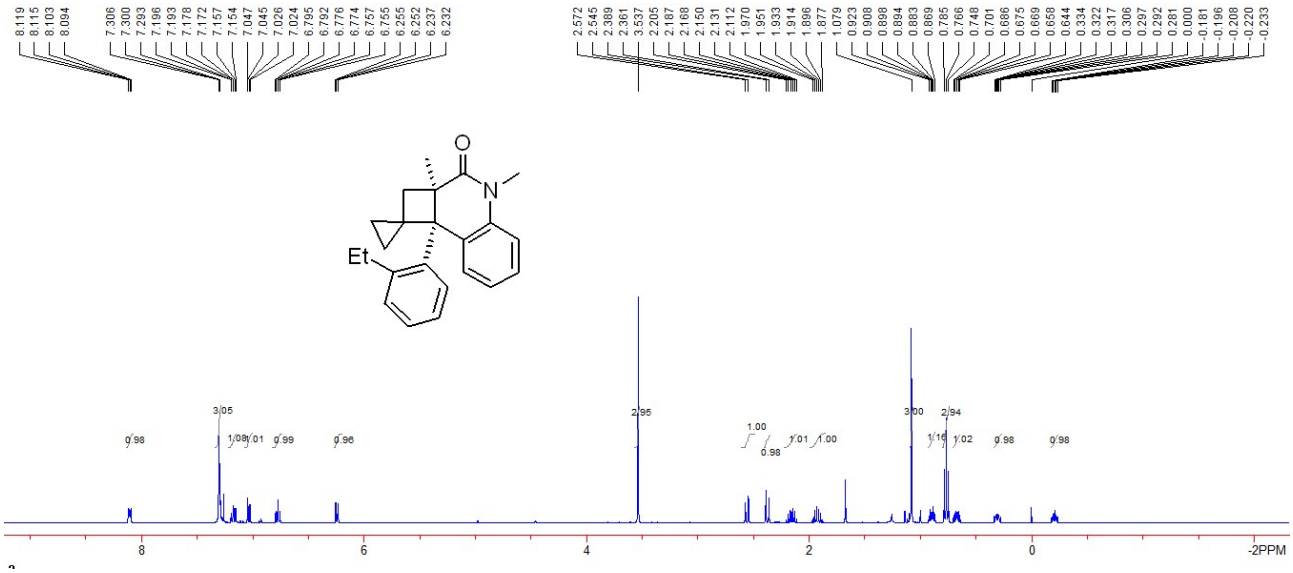


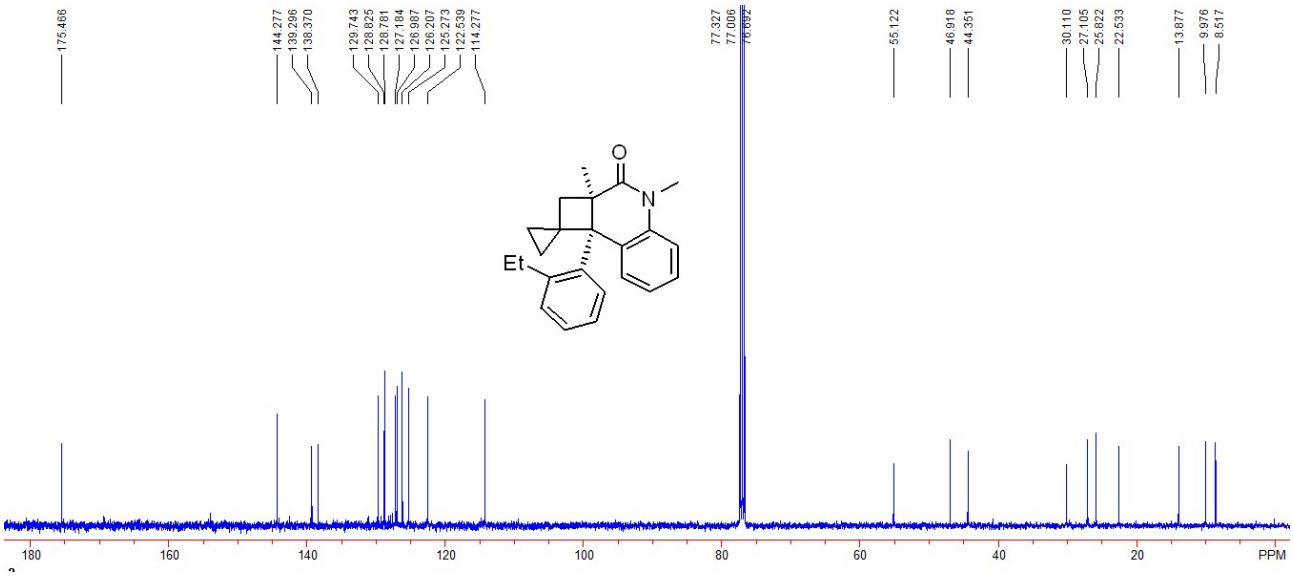


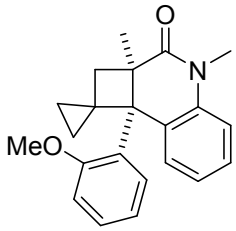


syn-8b-(2-ethylphenyl)-2a,4-Dimethyl-2,2a,4,8b-tetrahydro-3*H*-spiro[cyclobuta[*c*]quinoline-1,1'-cyclopropan]-3-one (3i)

pale green solid, 55 mg, 84% yield; *dr* > 20:1; m. p. 193 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.12-8.09 (m, 1H), 7.31-7.29 (m, 3H), 7.20-7.15 (m, 1H), 7.04 (dd, J_2 = 8.4 Hz, J_1 = 0.8 Hz, 1H), 6.78 (td, J_2 = 7.6 Hz, J_1 = 1.2 Hz, 1H), 6.24 (dd, J_2 = 7.2 Hz, J_1 = 1.6 Hz, 1H), 3.54 (s, 3H), 2.56 (d, J = 10.8 Hz, 1H), 2.38 (d, J = 11.2 Hz, 1H), 2.21-2.11 (m, 1H), 1.97-1.88 (m, 1H), 1.08 (s, 3H), 0.92-0.87 (m, 1H), 0.77 (t, J = 7.2 Hz, 3H), 0.70-0.64 (m, 1H), 0.33-0.28 (m, 1H), -0.18--0.23 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 175.5, 144.3, 139.3, 138.4, 129.7, 128.83, 128.78, 127.2, 127.0, 126.2, 125.3, 122.5, 114.3, 55.1, 46.9, 44.4, 30.1, 27.1, 25.8, 22.5, 13.9, 10.0, 8.5; IR (CH_2Cl_2): 2978, 2934, 1656, 1594, 1468, 1450, 1365, 1298, 1260, 1110, 1101, 991, 811, 750, 728, 665 cm^{-1}; HRMS (ESI) Calcd. For $C_{23}H_{26}NO$ $(M+H)^+$ requires: 332.2009, Found: 332.2003.

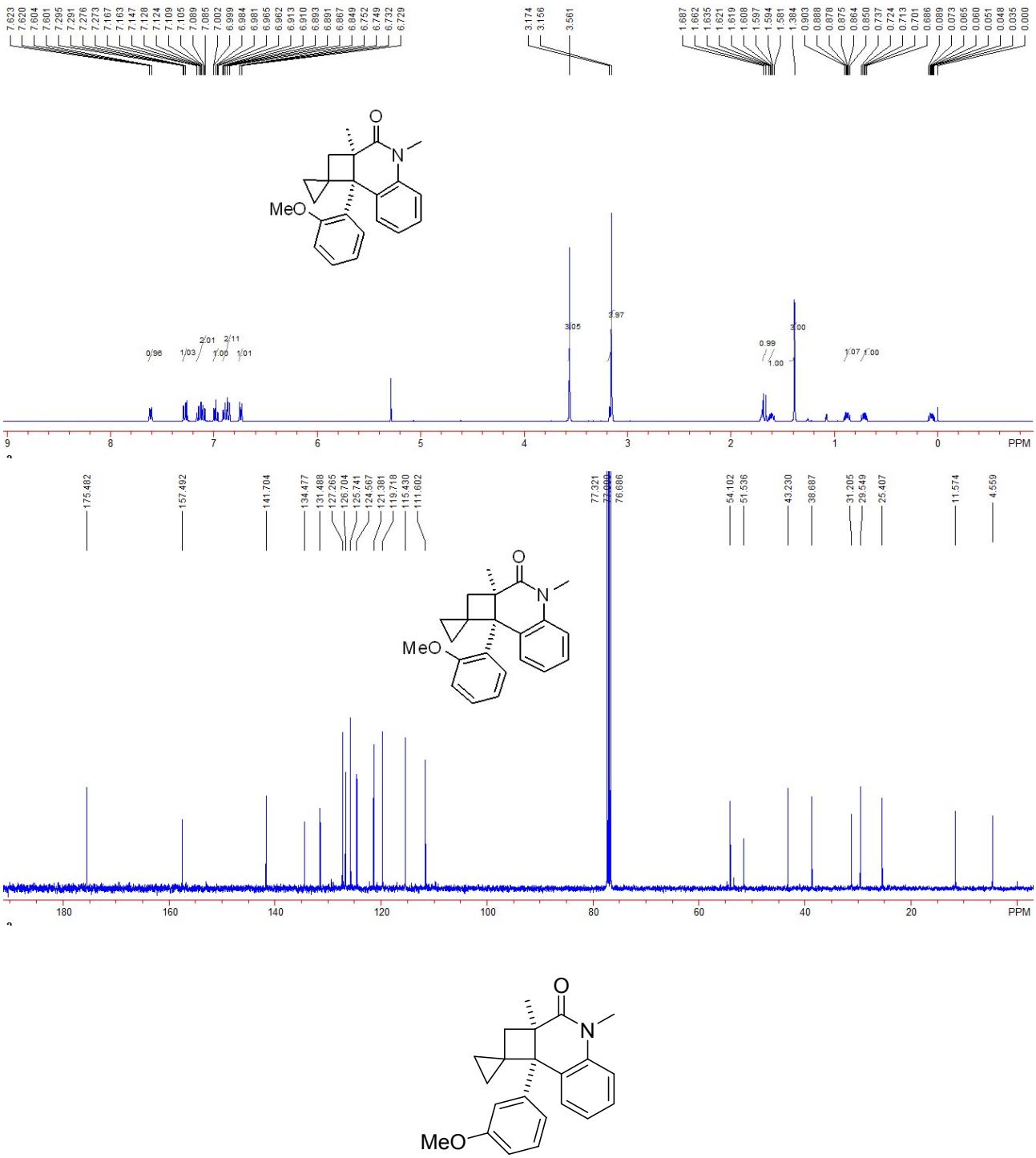






syn-8b-(2-methoxyphenyl)-2a,4-Dimethyl-2,2a,4,8b-tetrahydro-3*H*-spiro[cyclobuta[*c*]quinoline-1,1'-cyclopropan]-3-one (3j)

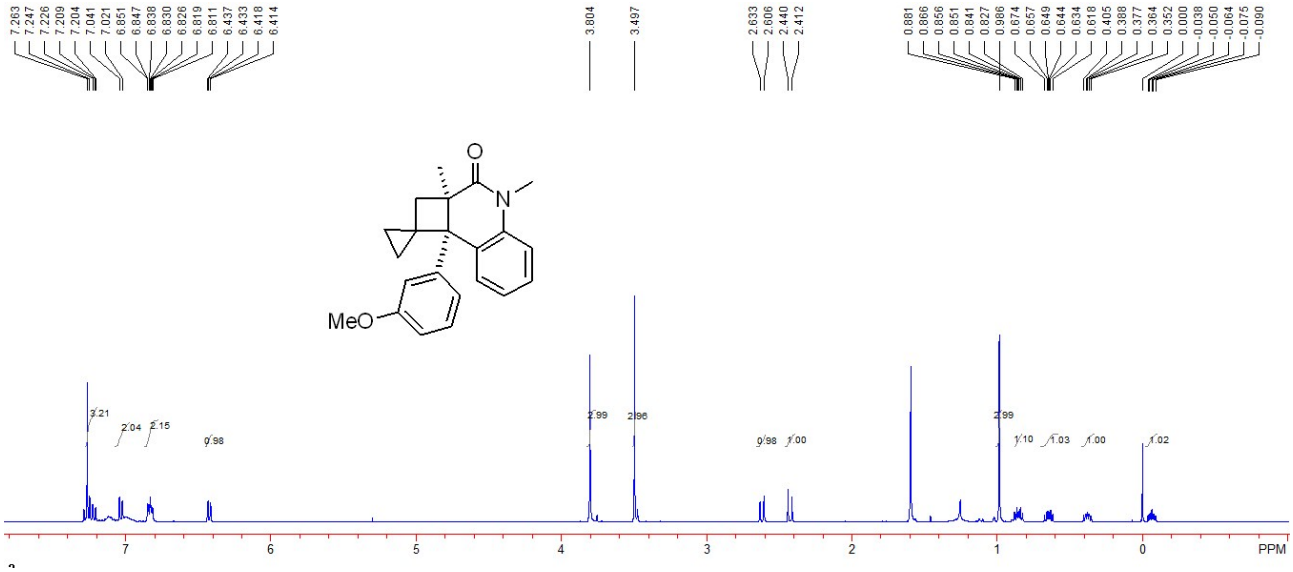
pale green solid, 57 mg, 86% yield; *dr* > 20:1; m. p. 190 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.61 (dd, J_2 = 7.6 Hz, J_1 = 1.2 Hz, 1H), 7.28 (dd, J_2 = 7.6 Hz, J_1 = 1.6 Hz, 1H), 7.18-7.09 (m, 2H), 6.98 (td, J_2 = 7.2 Hz, J_1 = 1.2 Hz, 1H), 6.91-6.85 (m, 1H), 6.74 (dd, J_2 = 8.0 Hz, J_1 = 1.2 Hz, 1H), 3.56 (s, 3H), 3.17-3.16 (m, 4H), 1.67 (d, J = 10.0 Hz, 1H), 1.64-1.58 (m, 1H), 1.38 (s, 3H), 0.90-0.85 (m, 1H), 0.74-0.69 (m, 1H), 0.09-0.04 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 175.5, 157.5, 141.7, 134.5, 131.5, 127.3, 126.7, 125.7, 124.6, 121.4, 119.7, 115.4, 111.6, 54.1, 51.5, 43.2, 38.7, 31.2, 29.5, 25.4, 11.6, 4.6; IR (CH_2Cl_2): 2974, 1676, 1593, 1467, 1450, 1435, 1414, 1295, 1247, 1223, 1076, 1061, 1045, 1033, 787, 770, 759, 680, 657 cm^{-1}; HRMS (ESI) Calcd. For $C_{22}H_{24}NO_2$ $(M+H)^+$ requires: 334.1802, Found: 334.1795.

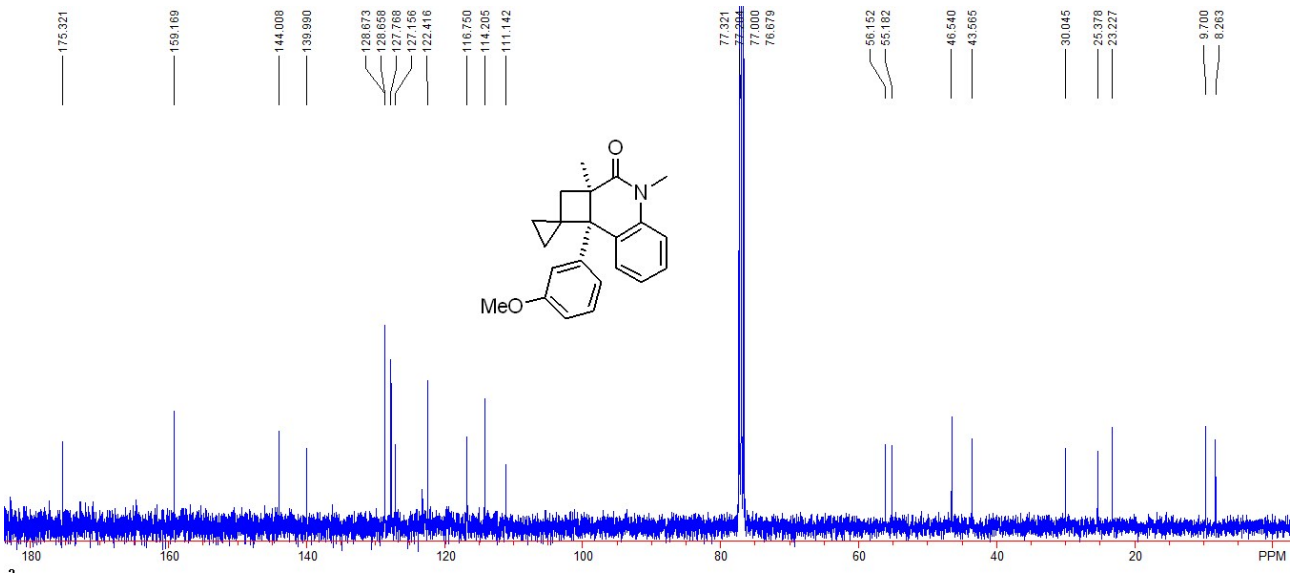


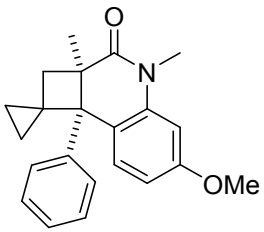
***syn*-8b-(3-methoxyphenyl)-2a,4-Dimethyl-2,2a,4,8b-tetrahydro-3*H*-spiro[cyclobuta[*c*]quinoline-1,1'-cyclopropan]-3-one (3k)**

pale green solid, 56 mg, 84% yield; *dr* > 20:1; m. p. 183 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.26-7.20 (m, 3H), 7.04-7.02 (m, 2H), 6.85-6.81 (m, 2H), 6.43 (dd, J_2 = 7.6 Hz, J_1 = 1.2 Hz, 1H), 3.80 (s, 3H), 3.50 (s, 3H), 2.62 (d, J = 10.8 Hz, 1H), 2.43 (d, J = 11.2 Hz, 1H), 0.99 (s, 3H), 0.88-0.83 (m, 1H), 0.67-0.62 (m, 1H), 0.41-0.35 (m, 1H), -0.04--0.09 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 175.3, 159.2, 144.0, 140.0, 128.67, 128.66, 127.8, 127.2, 122.4, 116.8, 114.2, 111.1,

56.2, 55.2, 46.5, 43.6, 30.0, 25.4, 23.2, 9.7, 8.3; IR (CH_2Cl_2): 2962, 2925, 1653, 1593, 1581, 1449, 1351, 1296, 1279, 1245, 1127, 1107, 1051, 805, 785, 750, 722, 707, 674 cm^{-1}; HRMS (ESI) Calcd. For $C_{22}H_{24}NO_2$ $(M+H)^+$ requires: 334.1802, Found: 334.1796.



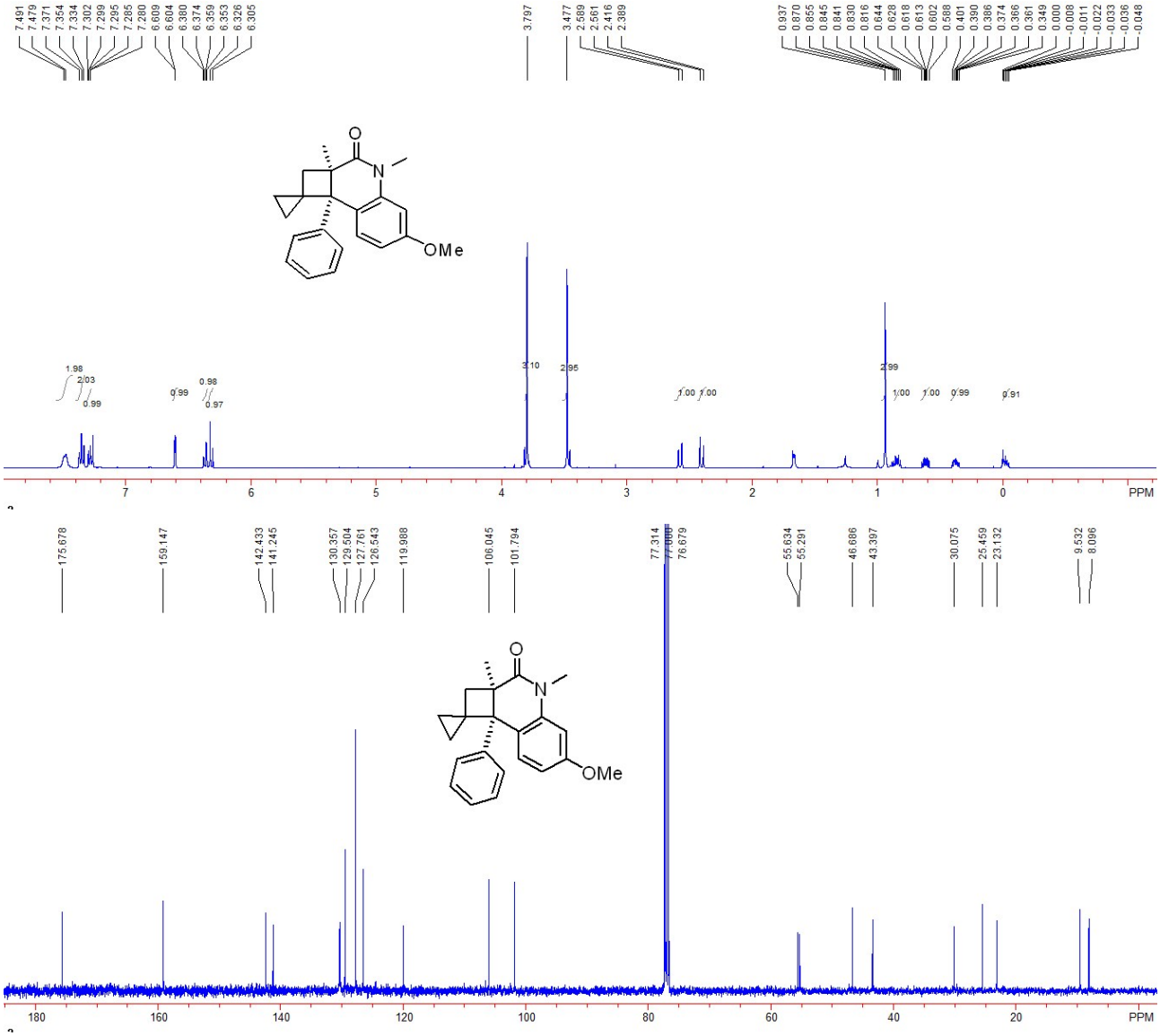


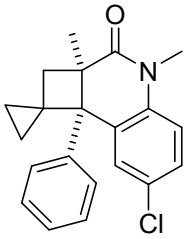


syn-6-Methoxy-2a,4-dimethyl-8b-phenyl-2,2a,4,8b-tetrahydro-3*H*-spiro[cyclobuta[*c*]quinoline-1,1'-cyclopropan]-3-one (3l)

pale green solid, 60 mg, 90% yield; *dr* > 20:1; m. p. 183 °C; ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 7.49-7.48 (m, 2H), 7.37-7.33 (m, 2H), 7.30-7.28 (m, 1H), 6.61 (d, J = 2.0 Hz, 1H), 6.37 (dd, J_2 =

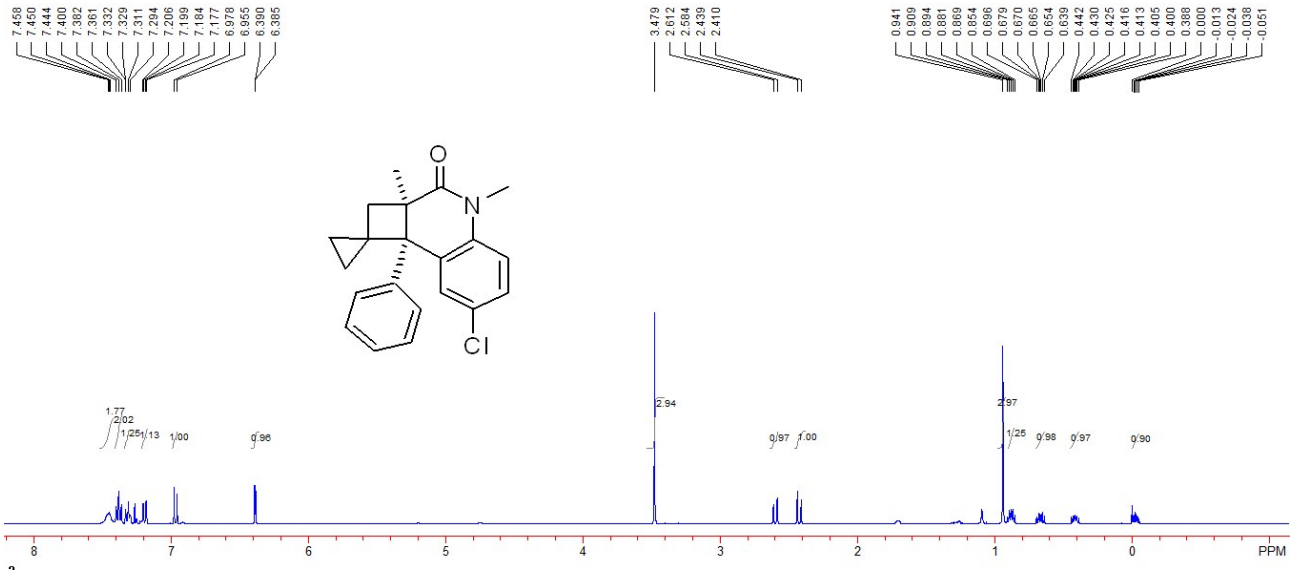
8.4 Hz, J_1 = 2.4 Hz, 1H), 6.32 (d, J = 8.4 Hz, 1H), 3.80 (s, 3H), 3.48 (s, 3H), 2.58 (d, J = 11.2 Hz, 1H), 2.40 (d, J = 10.8 Hz, 1H), 0.94 (s, 3H), 0.87-0.82 (m, 1H), 0.64-0.59 (m, 1H), 0.40-0.35 (m, 1H), -0.01--0.05 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 175.7, 159.1, 142.4, 141.2, 130.4, 129.5, 127.8, 126.5, 120.0, 106.0, 101.8, 55.6, 55.3, 46.7, 43.4, 30.1, 25.5, 23.1, 9.5, 8.1; IR (CH_2Cl_2): 2973, 2925, 1647, 1590, 1470, 1451, 1367, 1350, 1281, 1127, 1105, 1087, 1053, 1020, 785, 771, 761, 747, 657 cm^{-1}; HRMS (ESI) Calcd. For $C_{22}H_{24}NO_2$ $(M+H)^+$ requires: 334.1802, Found: 334.1795.

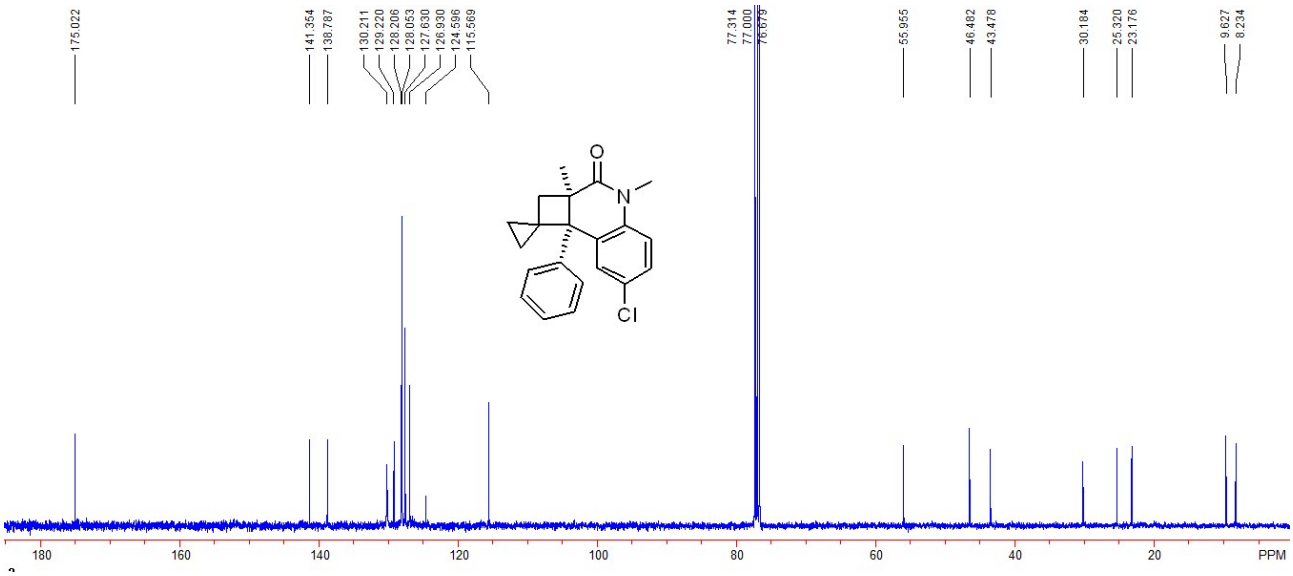


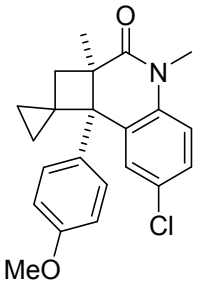


syn-7-Chloro-2a,4-dimethyl-8b-phenyl-2,2a,4,8b-tetrahydro-3H-spiro[cyclobuta[c]quinoline-1,1'-cyclopropan]-3-one (3m)

pale green solid, 60 mg, 89% yield; *dr* > 20:1; m. p. 180 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.46-7.44 (m, 2H), 7.40-7.36 (m, 2H), 7.33-7.29 (m, 1H), 7.19 (dd, J_2 = 8.8 Hz, J_1 = 2.8 Hz, 1H), 6.97 (d, *J* = 9.2 Hz, 1H), 6.39 (d, *J* = 2.0 Hz, 1H), 3.48 (s, 3H), 2.60 (d, *J* = 11.2 Hz, 1H), 2.42 (d, *J* = 11.6 Hz, 1H), 0.94 (s, 3H), 0.91-0.85 (m, 1H), 0.70-0.64 (m, 1H), 0.44-0.39 (m, 1H), -0.01--0.05 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 175.0, 141.4, 138.8, 130.2, 129.2, 128.2, 128.1, 127.6, 126.9, 124.6, 115.6, 56.0, 46.5, 43.5, 30.2, 25.3, 23.2, 9.6, 8.2; IR (CH_2Cl_2): 2978, 1649, 1566, 1496, 1392, 1322, 1243, 1217, 1096, 1017, 827, 788, 723, 688 cm^{-1}; HRMS (ESI) Calcd. For $C_{21}H_{21}ClNO$ $(M+H)^+$ requires: 338.1305, Found: 338.1302.

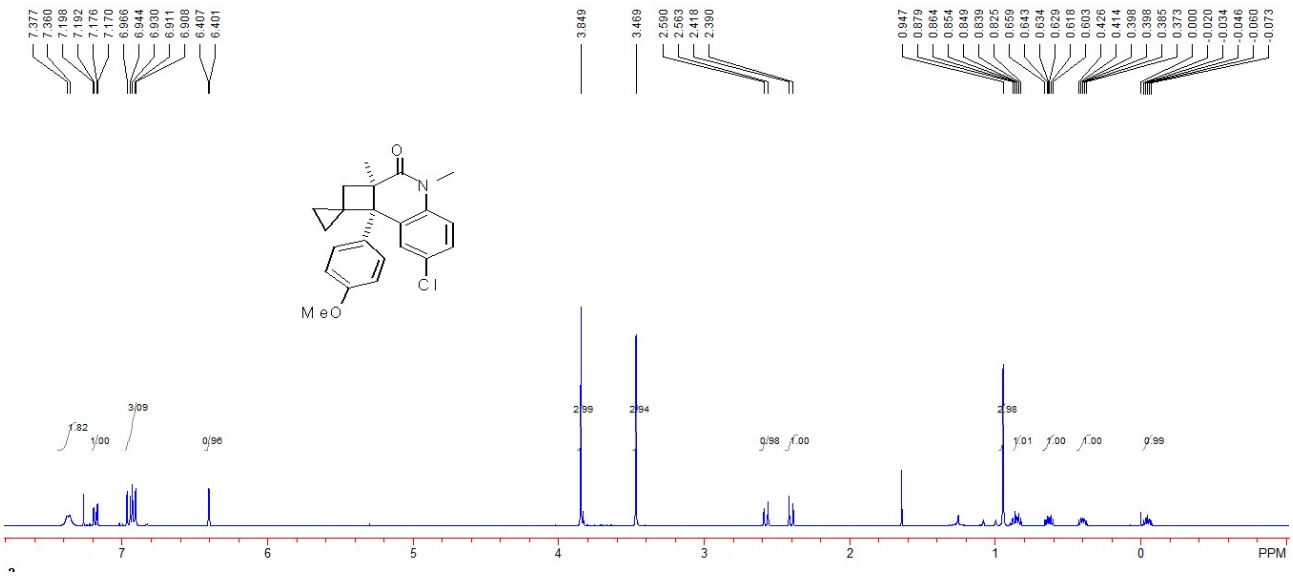


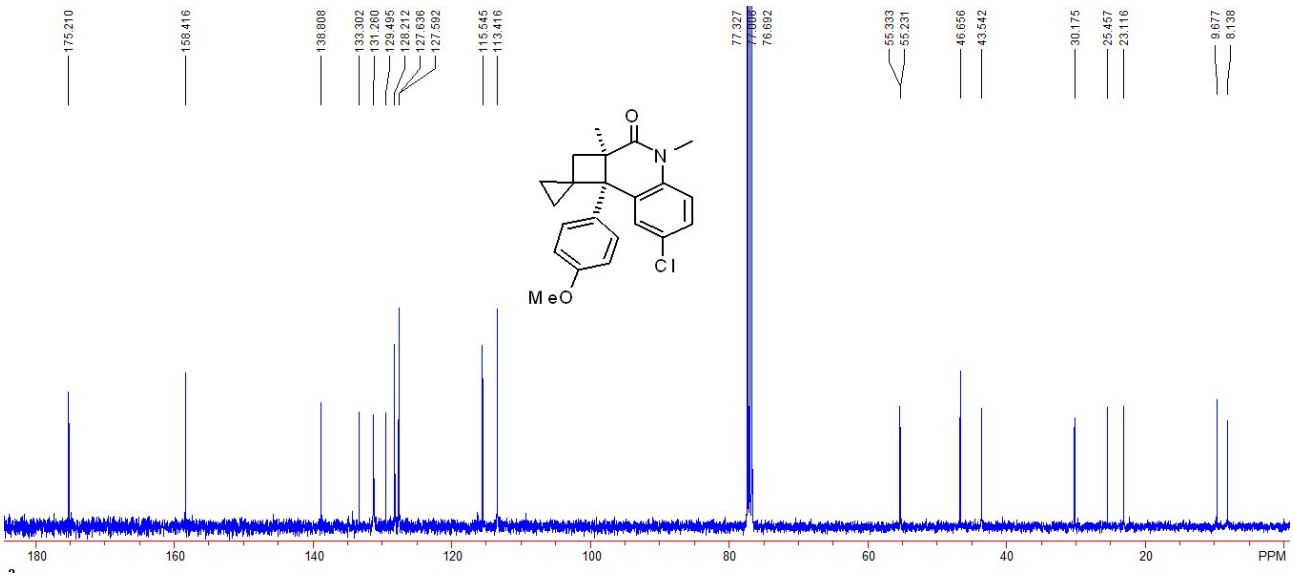


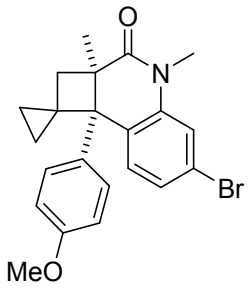


syn-7-Chloro-8b-(4-methoxyphenyl)-2a,4-dimethyl-2,2a,4,8b-tetrahydro-3*H*-spiro[cyclobuta[*c*]quinoline-1,1'-cyclopropan]-3-one (3n)

pale green solid, 67 mg, 91% yield; *dr* > 20:1; m. p. 179 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.38-7.36 (m, 2H), 7.18 (dd, J_2 = 8.8 Hz, J_1 = 2.4 Hz, 1H), 6.97-6.91 (m, 3H), 6.40 (d, J = 2.4 Hz, 1H), 3.85 (s, 3H), 3.47 (s, 3H), 2.58 (d, J = 10.8 Hz, 1H), 2.40 (d, J = 11.2 Hz, 1H), 0.95 (s, 3H), 0.85 (dt, J_1 = 6.0 Hz, J_2 = 10.0 Hz, 1H), 0.63 (dt, J_1 = 6.0 Hz, J_2 = 10.0 Hz, 1H), 0.43-0.37 (m, 1H), -0.02--0.07 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 175.2, 158.4, 138.8, 133.3, 131.3, 129.5, 128.2, 127.64, 127.59, 115.5, 113.4, 55.3, 55.2, 46.7, 43.5, 30.2, 25.5, 23.1, 9.7, 8.1; IR (CH_2Cl_2): 2957, 1647, 1591, 1496, 1458, 1363, 1350, 1305, 1275, 1248, 1115, 1086, 1032, 880, 817, 752, 726, 683 cm^{-1}; HRMS (ESI) Calcd. For $C_{22}H_{23}ClNO_2$ $(M+H)^+$ requires: 368.1412, Found: 368.1406.



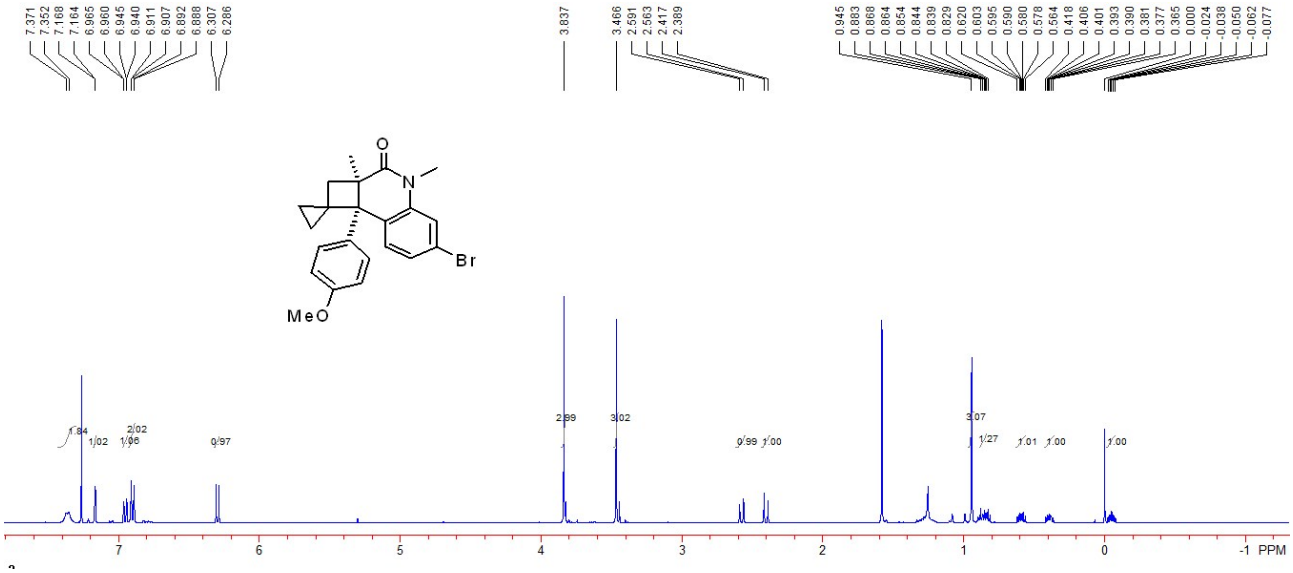


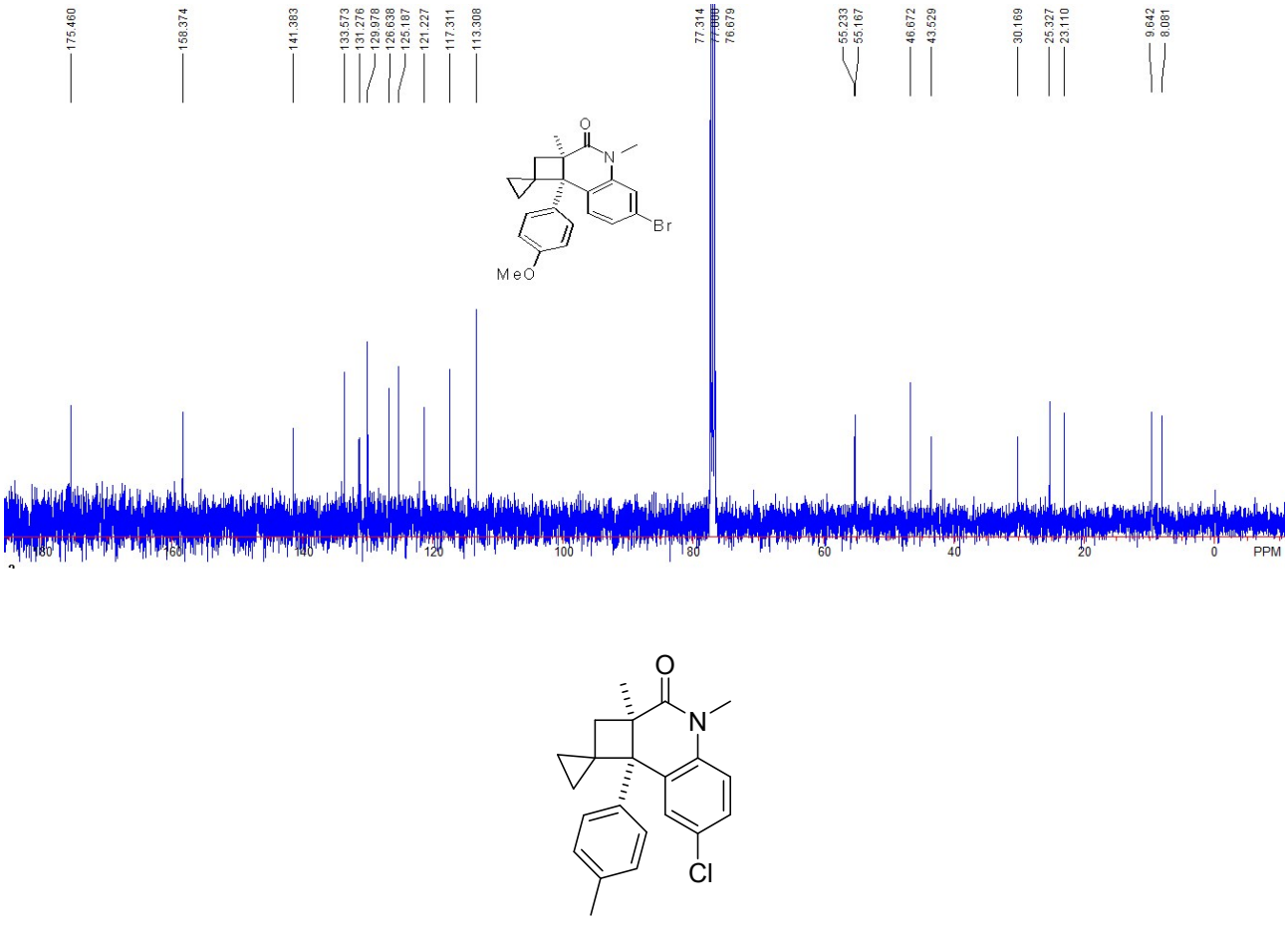


syn-6-Bromo-8b-(4-methoxyphenyl)-2a,4-dimethyl-2,2a,4,8b-tetrahydro-3*H*-spiro[cyclobuta[*c*]quinoline-1,1'-cyclopropan]-3-one (3o)

pale green solid, 77 mg, 94% yield; *dr* > 20:1; m. p. 189 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.37-7.35 (m, 2H), 7.17 (d, J = 1.6 Hz, 1H), 6.95 (dd, J_2 = 8.0 Hz, J_1 = 2.0 Hz, 1H), 6.91-6.89 (m, 2H), 6.30 (d, J = 8.4 Hz, 1H), 3.84 (s, 3H), 3.47 (s, 3H), 2.58 (d, J = 11.2 Hz, 1H), 2.40 (d, J = 11.2 Hz, 1H), 0.95 (s, 3H), 0.88-0.83 (m, 1H), 0.62-0.56 (m, 1H), 0.42-0.37 (m, 1H), -0.02--0.08 (m,

1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 175.5, 158.4, 141.4, 133.6, 131.3, 130.0, 126.6, 125.2, 121.2, 117.3, 113.3, 55.23, 55.17, 46.7, 43.5, 30.2, 25.3, 23.1, 9.6, 8.1; IR (CH_2Cl_2): 2970, 2921, 1655, 1585, 1507, 1494, 1459, 1407, 1333, 1307, 1265, 1242, 1178, 1127, 1106, 1032, 851, 824, 814, 802, 788, 768, 721 cm^{-1}; HRMS (ESI) Calcd. For $C_{22}H_{23}BrNO_2$ $(M+H)^+$ requires: 412.0907, Found: 412.0906.

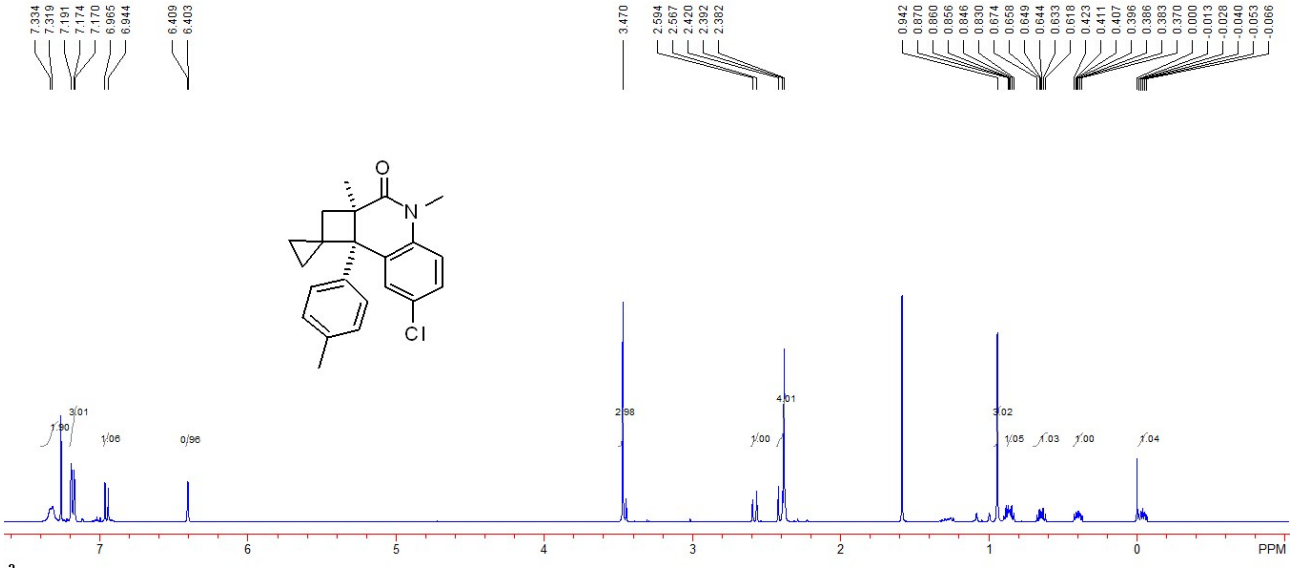


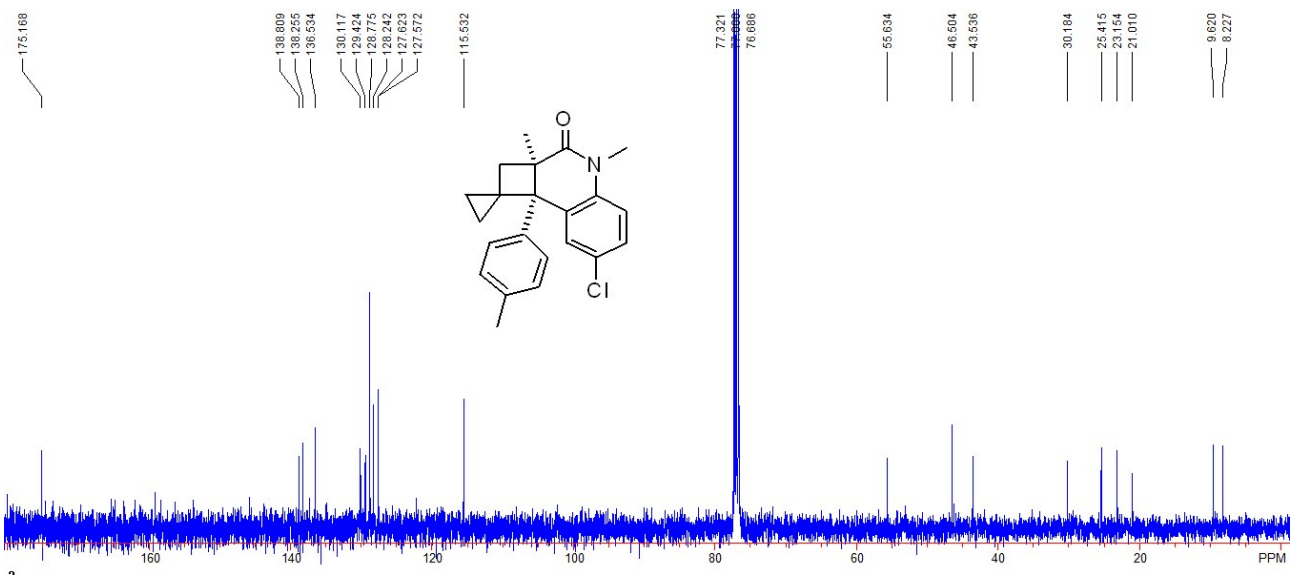


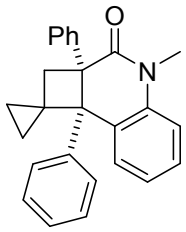
***syn*-7-Chloro-2a,4-dimethyl-8b-(p-tolyl)-2,2a,4,8b-tetrahydro-3*H*-spiro[cyclobuta[*c*]quinoline-**

1,1'-cyclopropan]-3-one (3p)

pale green solid, 59 mg, 85% yield; *dr* > 20:1; m. p. 180 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.33-7.32 (m, 2H), 7.19-7.17 (m, 3H), 6.95 (d, *J* = 8.8 Hz, 1H), 6.41 (d, *J* = 2.4 Hz, 1H), 3.47 (s, 3H), 2.58 (d, *J* = 10.8 Hz, 1H), 2.42-2.38 (m, 4H), 0.94 (s, 3H), 0.87-0.83 (m, 1H), 0.67-0.62 (m, 1H), 0.42-0.37 (m, 1H), -0.01--0.07 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 175.2, 138.8, 138.3, 136.5, 130.1, 129.4, 128.8, 128.2, 127.62, 127.57, 115.5, 55.6, 46.5, 43.5, 30.2, 25.4, 23.2, 21.0, 9.6, 8.2; IR (CH_2Cl_2): 2974, 1648, 1497, 1458, 1410, 1363, 1351, 1118, 1086, 1022, 881, 816, 804, 682, 668 cm^{-1}; HRMS (ESI) Calcd. For $C_{22}H_{23}ClNO$ $(M+H)^+$ requires: 352.1463, Found: 352.1457.

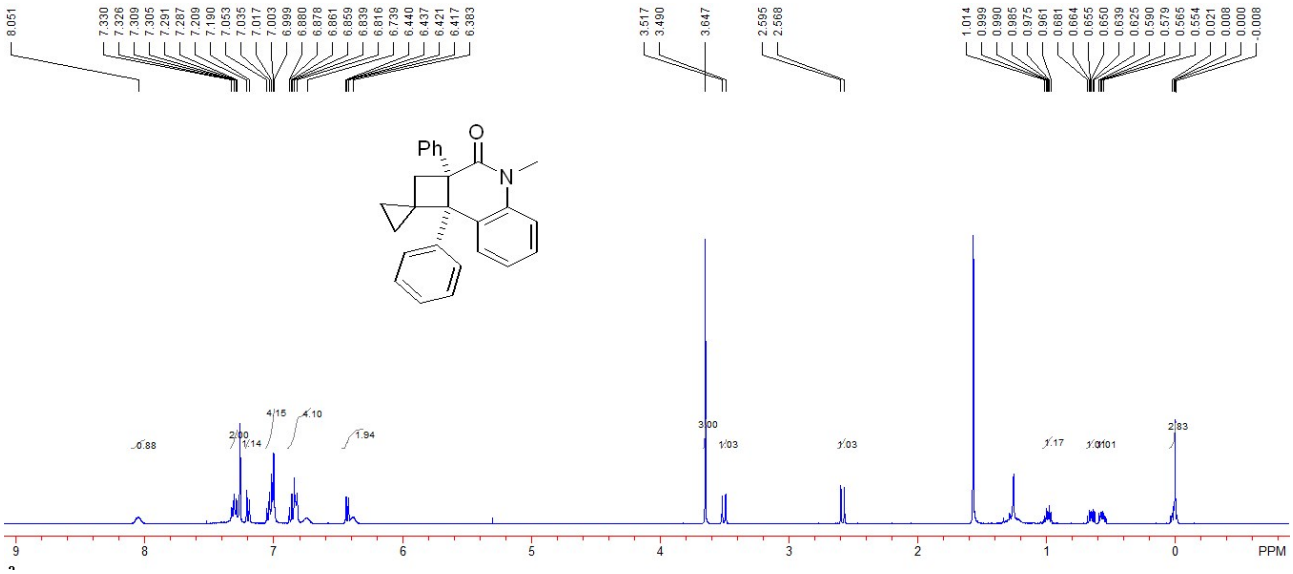


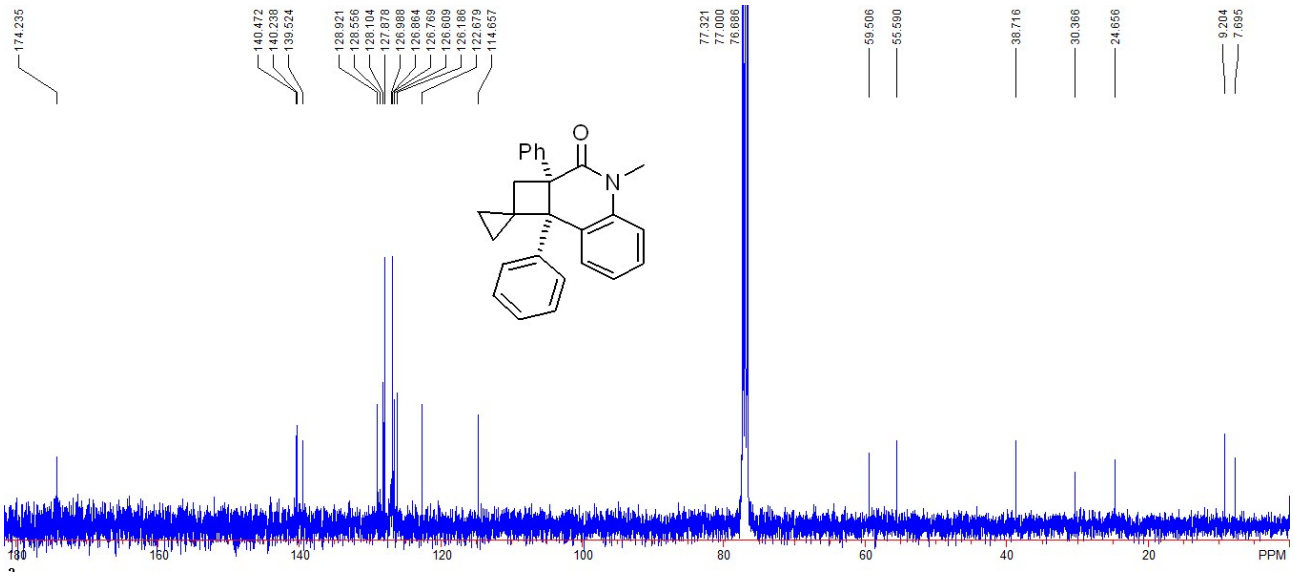


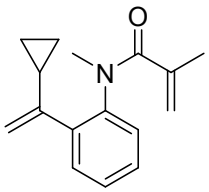


syn-4-Methyl-2a,8b-diphenyl-2,2a,4,8b-tetrahydro-3*H*-spiro[cyclobuta[*c*]quinoline-1,1'-cyclopropan]-3-one (3q)

pale green solid, 55 mg, 75% yield; *dr* > 20:1; m. p. 201 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.05 (s, 1H), 7.31 (td, J_2 = 8.4 Hz, J_1 = 1.6 Hz, 2H), 7.21-7.19 (m, 1H), 7.05-7.00 (m, 4H), 6.88-6.75 (m, 4H), 6.44-6.38 (m, 2H), 3.65 (s, 3H), 3.50 (d, J = 10.8 Hz, 1H), 2.58 (d, J = 10.4 Hz, 1H), 1.01-0.96 (m, 1H), 0.68-0.63 (m, 1H), 0.59-0.54 (m, 1H), 0.07--0.02 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 174.2, 140.5, 140.2, 139.5, 128.9, 128.6, 128.1, 127.9, 127.0, 126.9, 126.8, 126.6, 126.2, 122.7, 114.7, 59.5, 55.6, 38.7, 30.4, 24.7, 9.2, 7.7; IR (CH_2Cl_2): 2989, 2956, 1679, 1600, 1474, 1427, 1430, 1278, 1242, 1223, 1072, 1045, 1033, 777, 760, 723, 690, 677 cm^{-1}; HRMS (ESI) Calcd. For $C_{26}H_{24}NO$ $(M+H)^+$ requires: 366.1852, Found: 366.1845.

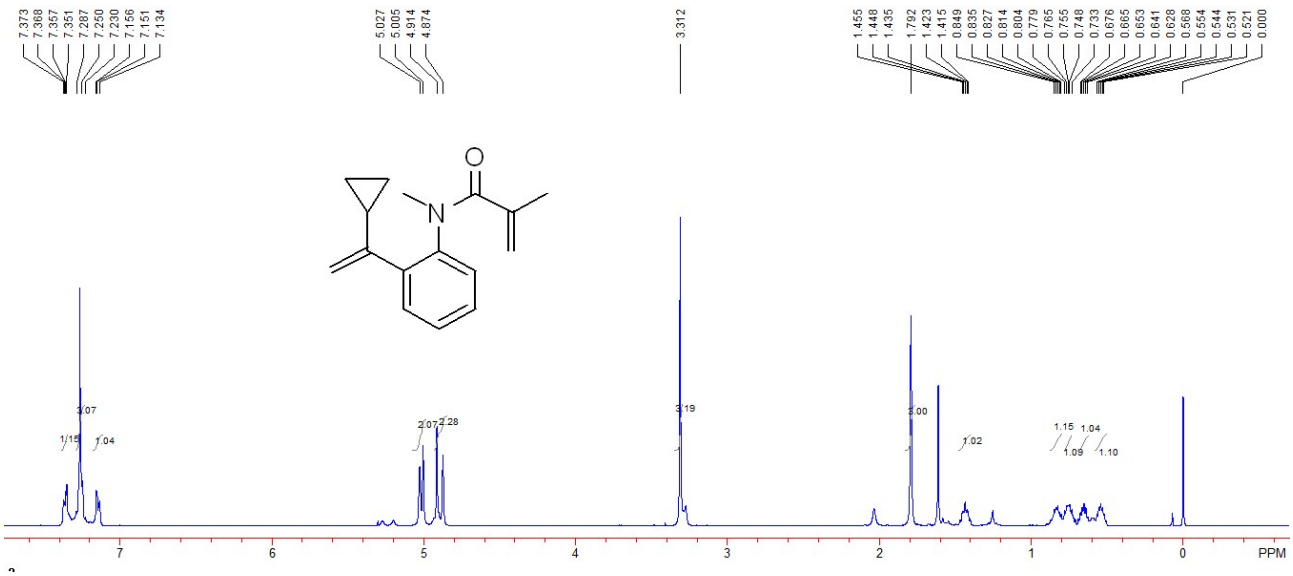






N-(2-(1-cyclopropylvinyl)phenyl)-N-methylmethacrylamide (4s)

Colorless oil, 41mg, 62% yield; m. p. 167 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.37-7.35 (m, 1H), 7.29-7.23 (m, 2H), 7.16-7.13 (m, 1H), 5.02 (d, J = 8.8 Hz, 2H), 4.89 (d, J = 16.0 Hz, 2H), 3.31 (s, 3H), 1.79 (s, 3H), 1.46-1.42 (m, 1H), 0.85-0.80 (m, 1H), 0.78-0.73 (m, 1H), 0.68-0.63 (m, 1H), 0.57-0.52 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 171.1, 148.4, 141.9, 140.5, 140.0, 130.0, 128.1, 128.0, 127.2, 120.2, 112.2, 38.1, 20.5, 16.2, 9.2, 6.6; IR (CH_2Cl_2): 2951, 2922, 1648, 1615, 1591, 1485, 1446, 1379, 1361, 1232, 1083, 1054, 1042, 946, 934, 893, 797, 775, 739 cm^{-1}; HRMS (ESI) Calcd. For $C_{19}H_{19}NO_2$ $(M+H)^+$ requires: 294.1489, Found: 294.1484.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5.005
4.914
4.874
3.312
1.455
1.448
1.435
1.792
1.423
1.415
0.849
0.835
0.827
0.814
0.804
0.779
0.765
0.755
0.748
0.733
0.676
0.665
0.653
0.641
0.628
0.568
0.554
0.544
0.531
0.521
0.000
O
N
3.07
1.15
1.04
2.07
2.28
3.19
3.00
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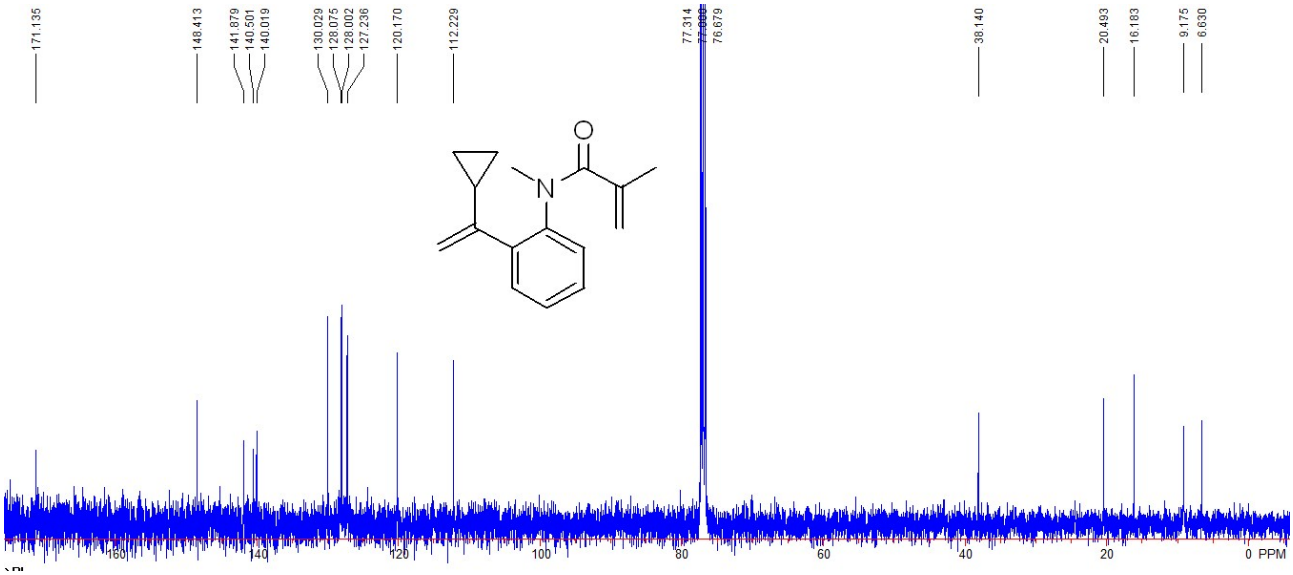
1.15
1.04
1.09
1.10
7
6
5
4
3
2
1
0
PPM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128.002
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112.229
77.314
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76.679
38.140
20.493
16.183
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140
120
100
80
60
40
20
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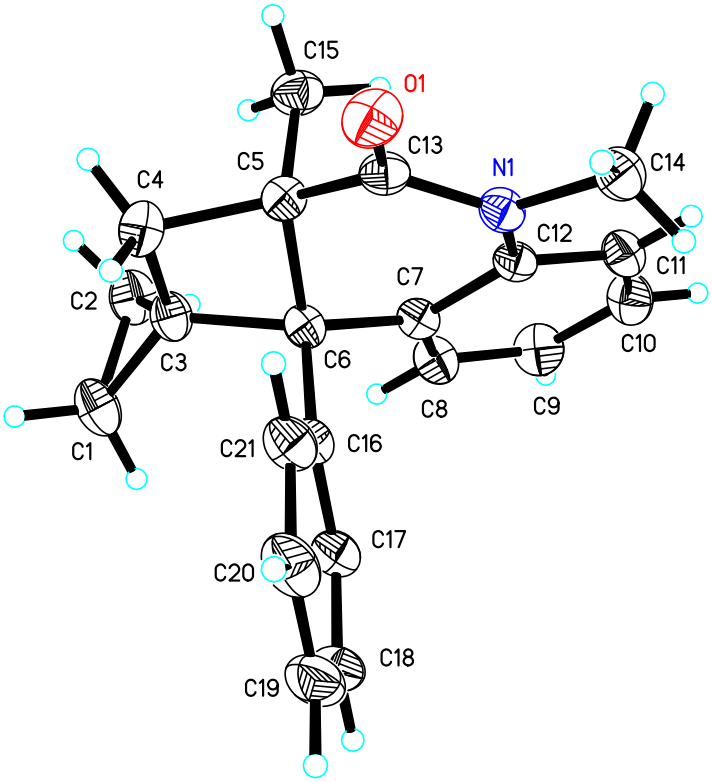
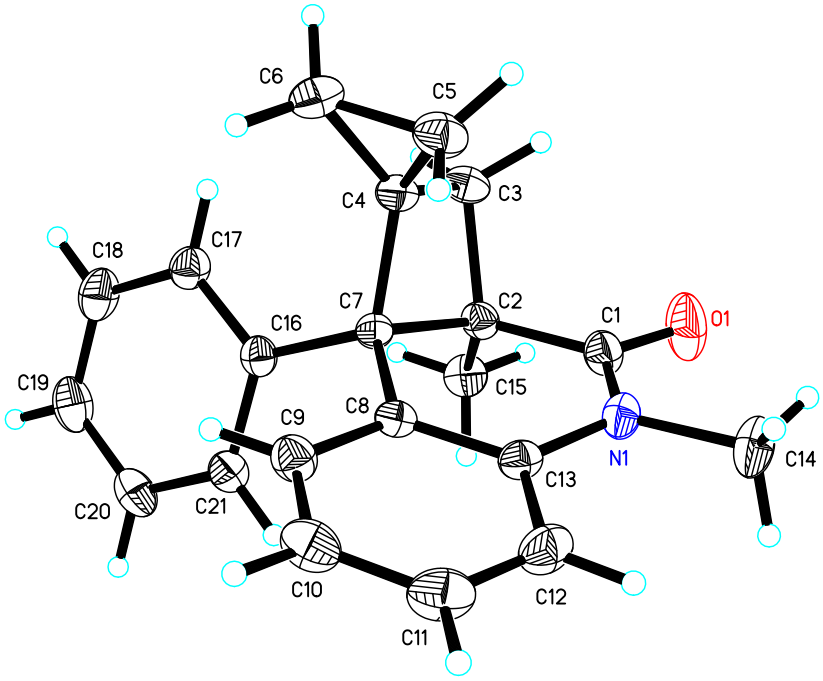
PPM

4. X-ray Data



The crystal data of **2a** have been deposited in CCDC with number 1569798. Empirical Formula: $C_{21}H_{21}NO$; Formula Weight: 303.39; Crystal Color, Habit: colorless; Crystal Dimensions: 0.220 x 0.170 x 0.130 mm^3; Crystal System: Orthorhombic; Lattice Parameters: a = 14.3887(13) Å, alpha = 90 deg. b = 9.1859(8) Å, beta = 90 deg. c = 24.515(2) Å, gamma = 90 deg; V = 3240.2(5) $Å^3$; Space group: P b c a; Z = 8; D_{calc} = 1.244 g/cm^3; F_{000} = 1296; Diffractometer: Rigaku AFC7R; Residuals: R; R_w: 0.0364, 0.0903.



The crystal data of **3a** have been deposited in CCDC with number 1579802. Empirical Formula: $C_{21}H_{21}NO$; Formula Weight: 303.39; Crystal Color, Habit: colorless; Crystal Dimensions: 0.200 x 0.160 x 0.110 mm^3; Crystal System: Triclinic; Lattice Parameters: a = 9.4746(4) Å, alpha = 78.0810(10) deg. b = 9.4905(4) Å, beta = 70.1660(10) deg. c = 9.7931(4) Å, gamma = 77.5270(10) deg; V = 800.24(6) $Å^3$; Space group: P -1; Z = 2; D_{calc} = 1.259 g/cm^3; F_{000} = 324; Diffractometer: Rigaku AFC7R; Residuals: R; R_w: 0.0454, 0.1083.

5. Computational Details

The geometries of all species have been optimized at M06/6-31G(d) level. The subsequent frequency calculations on the stationary points were carried out at the same level of theory to ascertain the nature of the stationary points as minima or first-order saddle points on the respective potential energy surfaces. All transition states were characterized by one and only one imaginary frequency pertaining to the desired reaction coordinate. The intrinsic reaction coordinate (IRC) calculations were carried out at the same level of theory to further authenticate the transition states. Thermochemical corrections to 298.15 K have been calculated for all minima from unscaled vibrational frequencies obtained at this same level. The conformational space of flexible systems has first been searched manually. The solvent effect was estimated by the IEFPCM method with radii and non-electrostatic terms for SMD salvation model in *o*-dichlorobenzene (ε = 9.9949), and solvation single-point computations were calculated at M06/6-311+G(d,p) level. All quantum mechanical calculations have been performed with Gaussian 016.

Table SI-1

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2a	-942.3674951	-941.979541	-942.0447658
TS1'	-942.2345899	-941.853275	-941.9210836
3a	-942.3923126	-942.004017	-942.0699931

Archive entries

1a

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2a

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TS1′

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3a

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,10.4196677,-7.8424948,-2.4165611,-5.7968792,2.6386311\PG=C01 [X(C21H2
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