Supporting Information

Copper(I)-catalyzed carbocyclization of acrylamide-tethered alkylidenecyclopropanes with diaryliodonium salts

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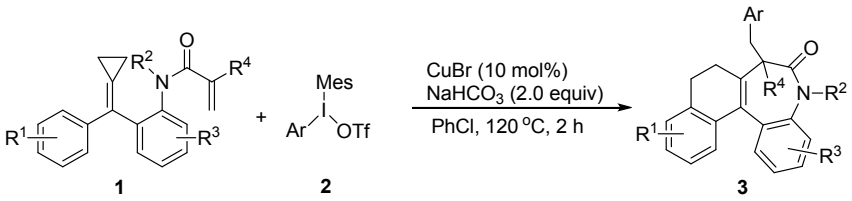
CONTENTS

1. General Remarks.

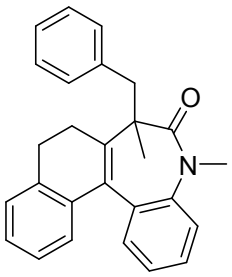
Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. NMR spectra were recorded with a Bruker spectrometer at 400 MHz (^{1}H NMR), 100 MHz (^{13}C NMR) and 376 MHz (^{19}F NMR) in $CDCl_3$, respectively. Chemical shift were reported in ppm down field from 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**-**1u** were prepared and characterized according to the procedure in the previous literature.[1] The unsymmetrical diaryl iodonium salts **2** that are used in this reaction can be readily prepared in a one-pot procedure from the corresponding aryl iodide and mesitylene according to the previous literature.[2]

2. General Procedure for the Synthesis of 3.



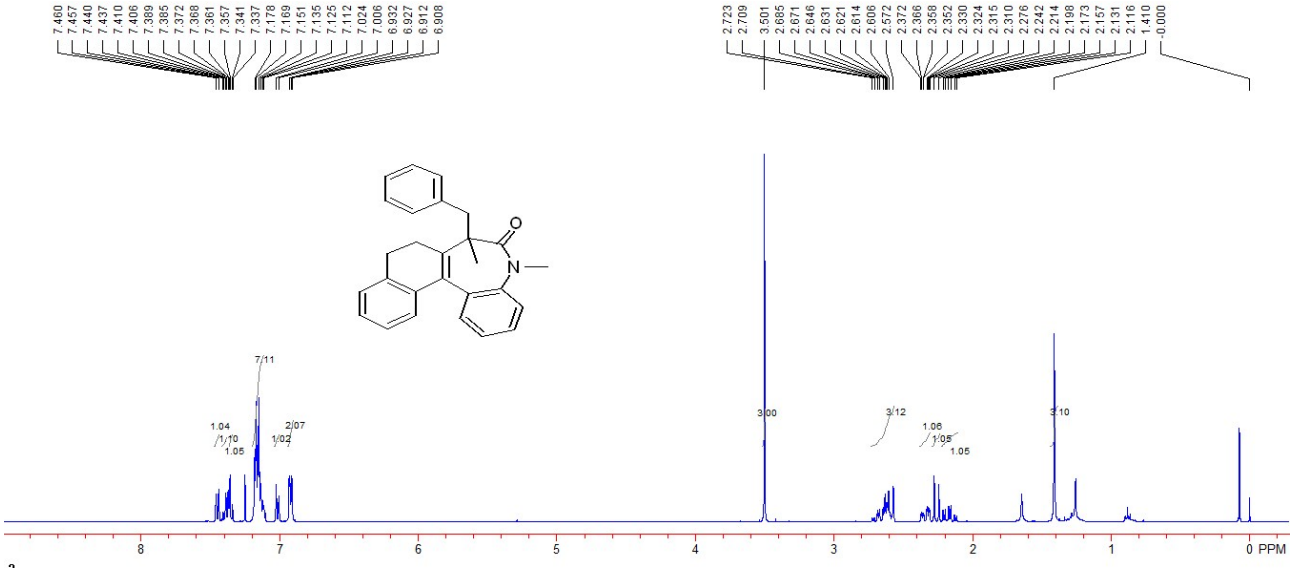
Compound **1** (0.20 mmol), diaryl iodonium salt **2** (0.40 mmol), CuBr (0.02 mmol), $NaHCO_3$ (0.40 mmol) were added to a Schlenk tube with a magnetic bar. PhCl (2.0 mL) was added and the reaction tube was heated to 120 °C for 2 h. The reaction mixture was concentrated in vacuum, and the resulting residue was purified by a silica gel chromatography (eluent: petroleum ether / ethyl acetate = 10:1) to afford the desired product **3**.

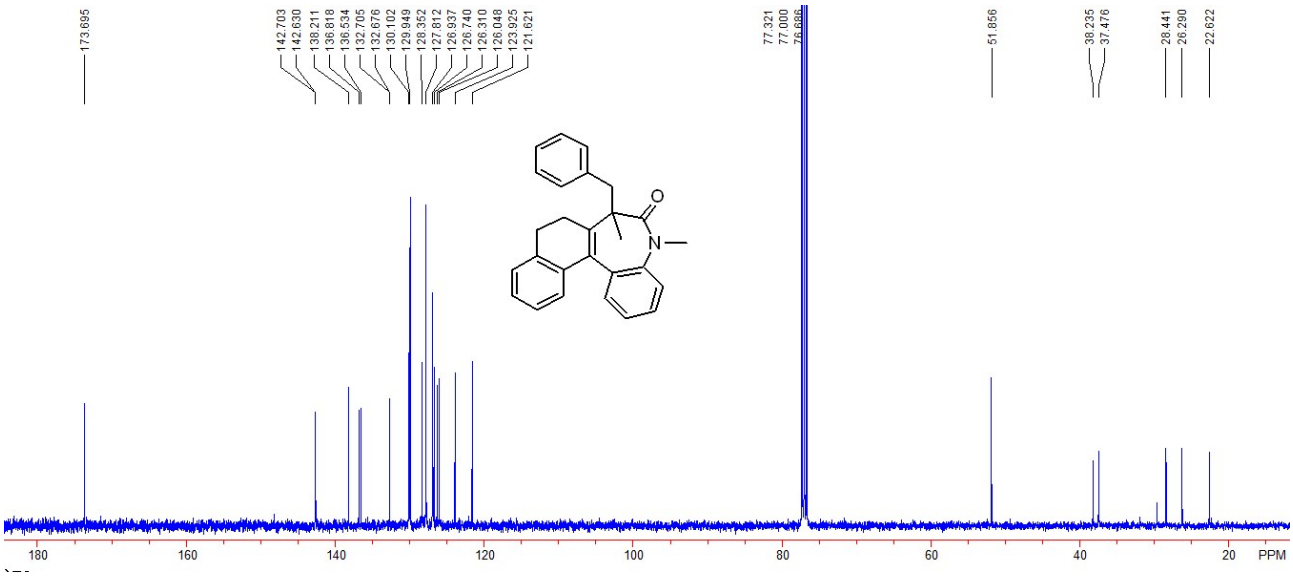
3. The characterization data of products

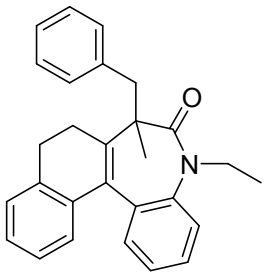


7-Benzyl-5,7-dimethyl-5,7,8,9-tetrahydro-6*H*-benzo[*b*]naphtho[1,2-*d*]azepin-6-one (3aa)

pale green solid, 65 mg, 85% yield; m. p. 220 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.45 (dd, J_1 = 1.2 Hz, J_2 = 8.0 Hz, 1H), 7.41-7.37 (m, 1H), 7.35 (dd, J_1 = 1.2 Hz, J_2 = 8.0 Hz, 1H), 7.18-7.11 (m, 7H), 7.02 (d, J = 7.2 Hz, 1H), 6.92 (dd, J_1 = 2.0 Hz, J_2 = 8.0 Hz, 2H), 3.50 (s, 3H), 2.72-2.57 (m, 3H), 2.34 (ddd, J_1 = 2.4 Hz, J_2 = 5.6 Hz, J_3 = 16.8 Hz, 1H), 2.26 (d, J = 13.6 Hz, 1H), 2.17 (td, J_1 = 6.4 Hz, J_2 = 16.4 Hz, 1H), 1.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 173.7, 142.7, 142.6, 138.2, 136.8, 136.5, 132.71, 132.68, 130.1, 129.9, 128.4, 127.8, 126.9, 126.7, 126.3, 126.0, 123.9, 121.6, 51.9, 38.2, 37.5, 28.4, 26.3, 22.6; IR (CH_2Cl_2): ν 2958, 2923, 1652, 1455, 1408, 1394, 1379, 1250, 1066, 1057, 1028, 880, 804, 783, 763, 728, 721, 668 cm^{-1}; HRMS (ESI) Calcd. For $C_{27}H_{26}NO$ $(M+H)^+$ requires: 380.2009, Found: 380.2001.

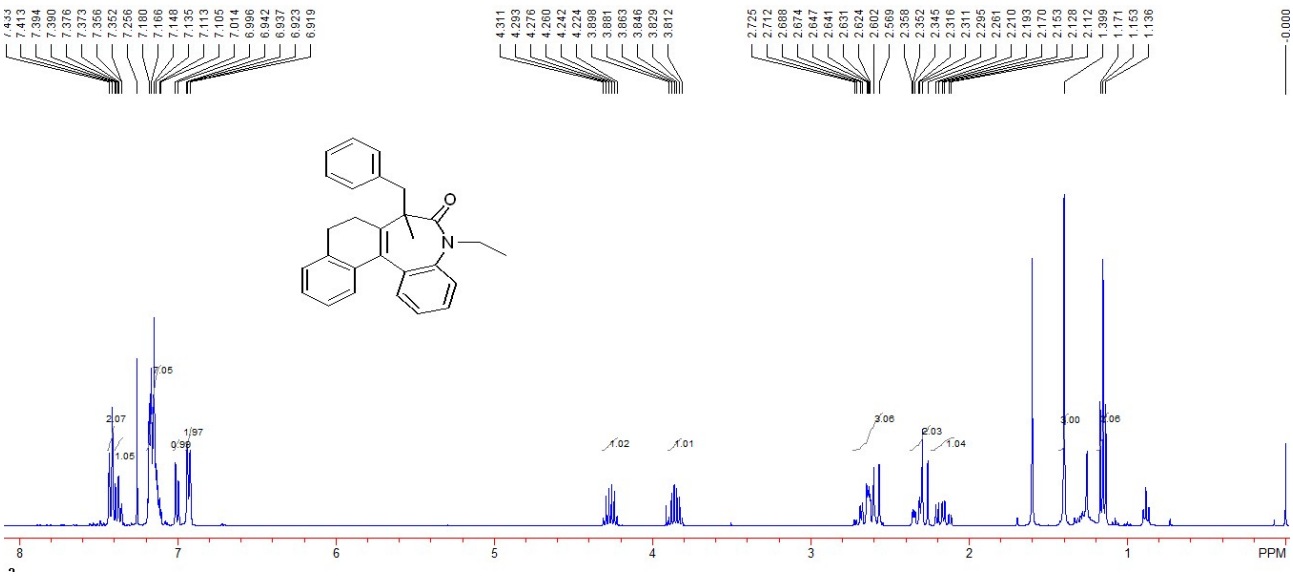


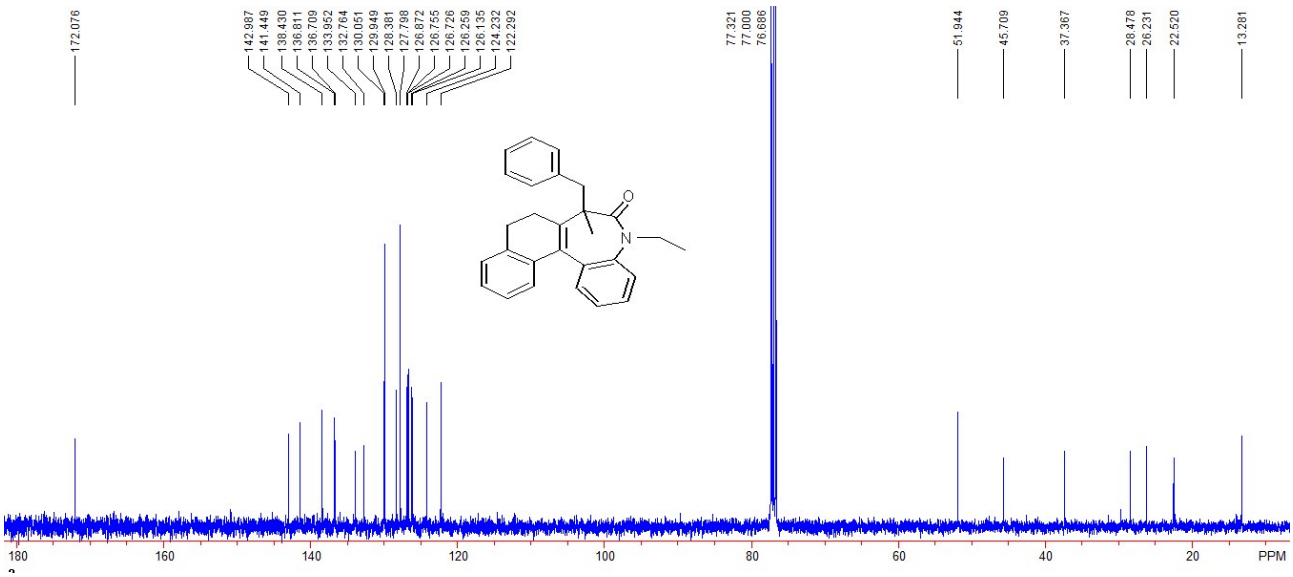


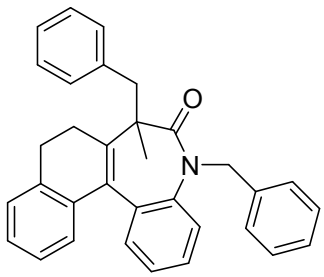


7-Benzyl-5-ethyl-7-methyl-5,7,8,9-tetrahydro-6*H*-benzo[*b*]naphtho[1,2-*d*]azepin-6-one (3ab)

pale green solid, 55 mg, 70% yield; m. p. 220 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.42 (d, J = 7.6 Hz, 2H), 7.37 (td, J_1 = 1.6 Hz, J_2 = 7.2 Hz, 1H), 7.26-7.11 (m, 7H), 7.01 (d, J = 7.2 Hz, 1H), 6.94-6.92 (m, 2H), 4.31-4.22 (m, 1H), 3.90-3.81 (m, 1H), 2.73-2.57 (m, 3H), 2.36-2.26 (m, 2H), 2.16 (td, J_1 = 6.8 Hz, J_2 = 16.0 Hz, 1H), 1.40 (s, 3H), 1.15 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 172.1, 143.0, 141.4, 138.4, 136.8, 136.7, 134.0, 132.8, 130.1, 129.9, 128.4, 127.8, 126.9, 126.8, 126.7, 126.3, 126.1, 124.2, 122.3, 51.9, 45.7, 37.4, 28.5, 26.2, 22.5, 13.3; IR (CH_2Cl_2): ν 2988, 2901, 1644, 1596, 1494, 1446, 1378, 1248, 1230, 1078, 1066, 1050, 765, 750, 728, 699, 669, 653 cm^{-1}; HRMS (ESI) Calcd. For $C_{28}H_{28}NO$ $(M+H)^+$ requires: 394.2165, Found: 394.2158.



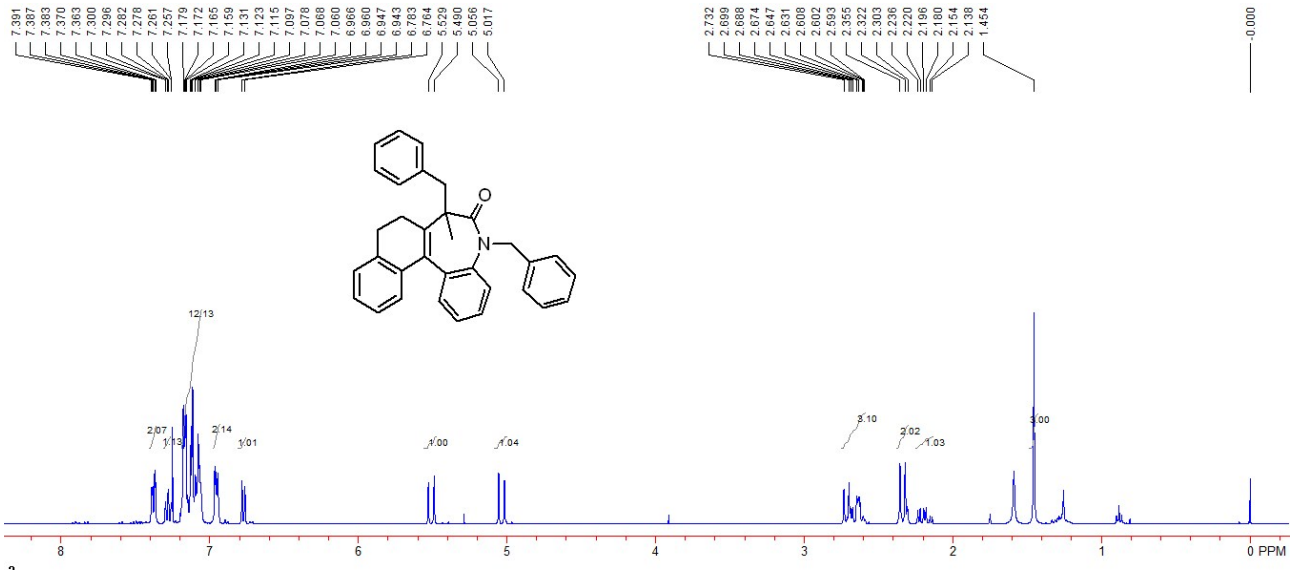


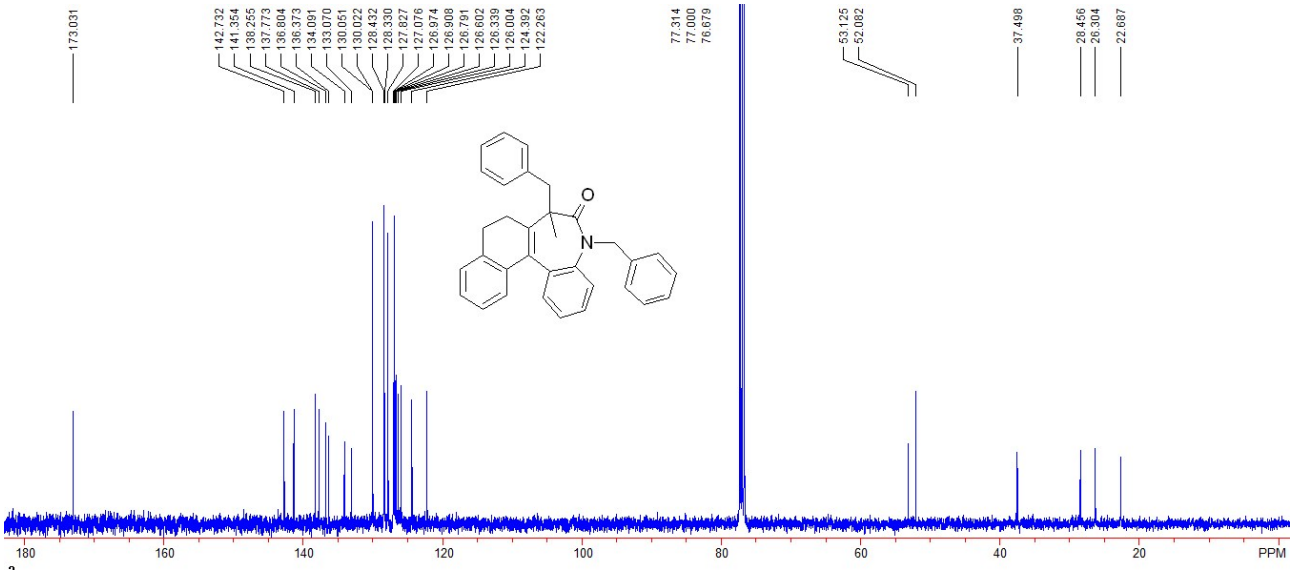


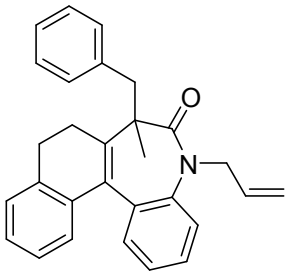
5,7-Dibenzyl-7-methyl-5,7,8,9-tetrahydro-6*H*-benzo[*b*]naphtho[1,2-*d*]azepin-6-one (3ac)

pale green solid, 67 mg, 73% yield; m. p. 200 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.39-7.36 (m, 2H), 7.28 (td, J_1 = 1.6 Hz, J_2 = 7.2 Hz, 1H), 7.18-7.06 (m, 12H), 6.97-6.94 (m, 2H), 6.77 (d, J = 7.6 Hz, 1H), 5.51 (d, J = 15.6 Hz, 1H), 5.04 (d, J = 15.6 Hz, 1H), 2.73-2.59 (m, 3H), 2.36-2.30 (m, 2H), 2.19 (td, J_1 = 6.4 Hz, J_2 = 16.0 Hz, 1H), 1.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ

173.0, 142.7, 141.4, 138.3, 137.8, 136.8, 136.4, 134.1, 133.1, 130.1, 130.0, 128.4, 128.3, 127.8, 127.1, 127.0, 126.9, 126.8, 126.6, 126.3, 126.0, 124.4, 122.3, 53.1, 52.1, 37.5, 28.5, 26.3, 22.7; IR (CH_2Cl_2): ν 2970, 2918, 1647, 1494, 1447, 1378, 1249, 1079, 1066, 1057, 1028, 767, 748, 728, 697, 668, 653 cm^{-1}; HRMS (ESI) Calcd. For $C_{33}H_{30}NO$ $(M+H)^+$ requires: 456.2322, Found: 456.2318.

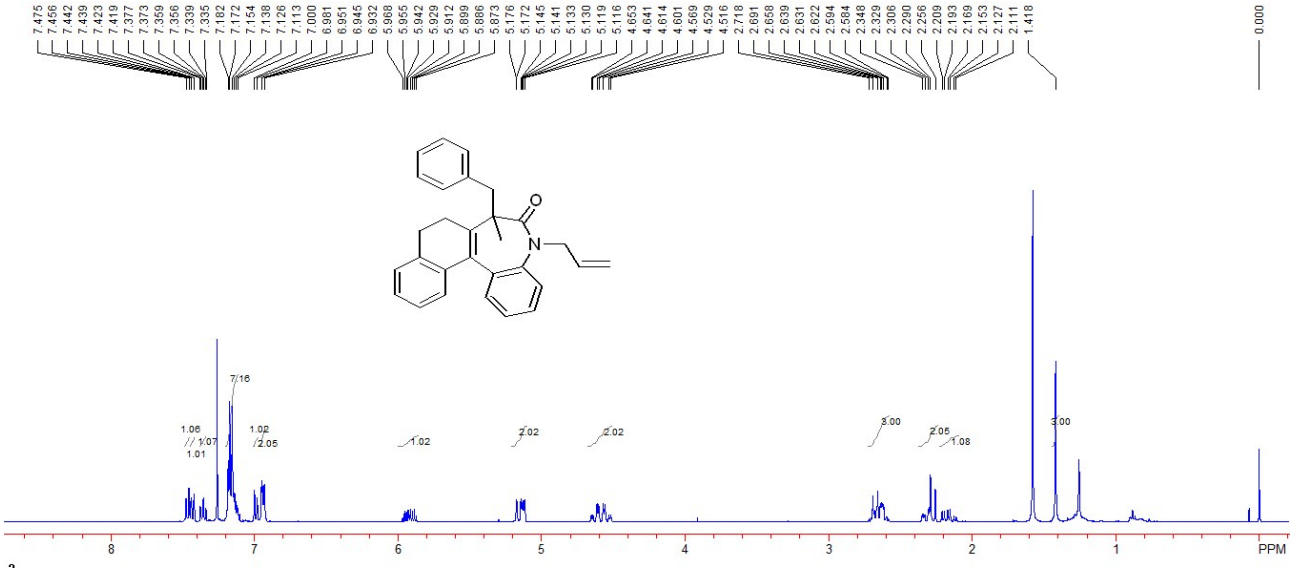


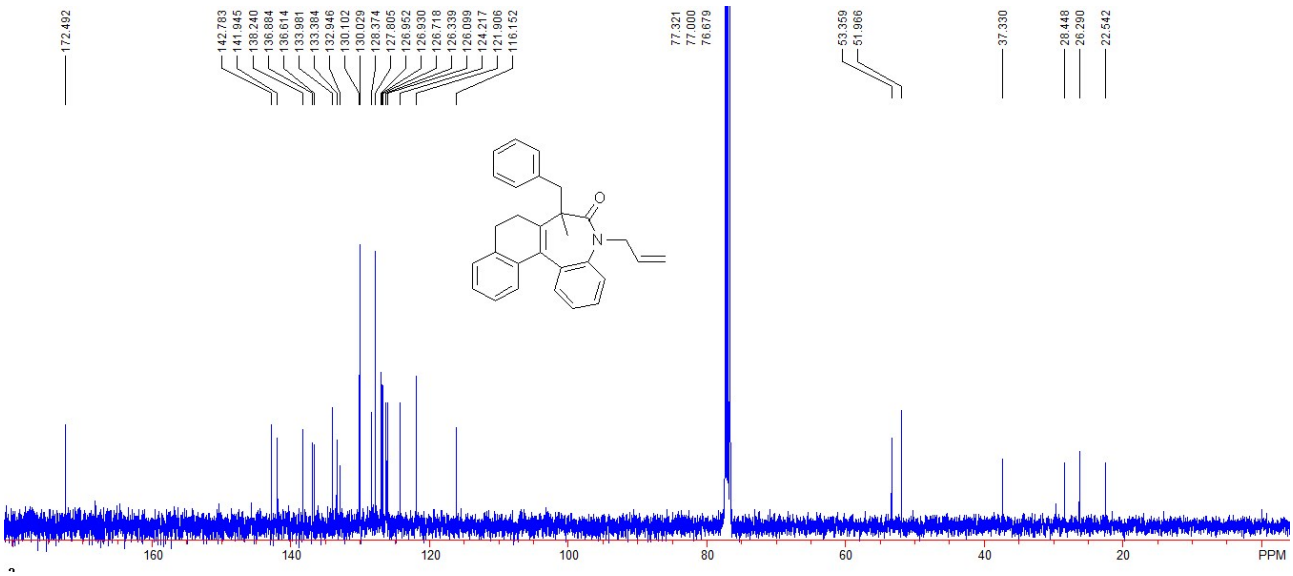


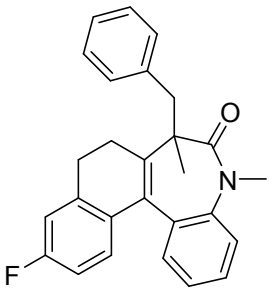


5-Allyl-7-benzyl-7-methyl-5,7,8,9-tetrahydro-6*H*-benzo[*b*]naphtho[1,2-*d*]azepin-6-one (3ad)

pale green solid, 55 mg, 68% yield; m. p. 243 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.46 (d, J = 5.6 Hz, 1H), 7.43 (dd, J_1 = 1.2 Hz, J_2 = 8.0 Hz, 1H), 7.36 (td, J_1 = 1.6 Hz, J_2 = 7.2 Hz, 1H), 7.18-7.11 (m, 7H), 6.99 (d, J = 7.6 Hz, 1H), 6.95-6.93 (m, 2H), 5.92 (ddd, J_1 = 5.2 Hz, J_2 = 10.4 Hz, J_3 = 22.4 Hz, 1H), 5.18-5.12 (m, 2H), 4.65-4.52 (m, 2H), 2.72-2.58 (m, 2H), 2.35-2.26 (m, 2H), 2.16 (td, J_1 = 6.4 Hz, J_2 = 16.0 Hz, 1H), 1.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 172.5, 142.8, 141.9, 138.2, 136.9, 136.6, 134.0, 133.4, 132.9, 130.1, 130.0, 128.4, 127.8, 127.0, 126.9, 126.7, 126.3, 126.1, 124.2, 121.9, 116.2, 53.4, 52.0, 37.3, 28.4, 26.3, 22.5; IR (CH_2Cl_2): ν 2926, 2854, 1644, 1594, 1448, 1390, 1361, 1250, 1187, 1164, 1132, 1110, 1056, 876, 767, 750, 729, 668, 653 cm^{-1}; HRMS (ESI) Calcd. For $C_{29}H_{28}NO$ $(M+H)^+$ requires: 406.2165, Found: 406.2166.

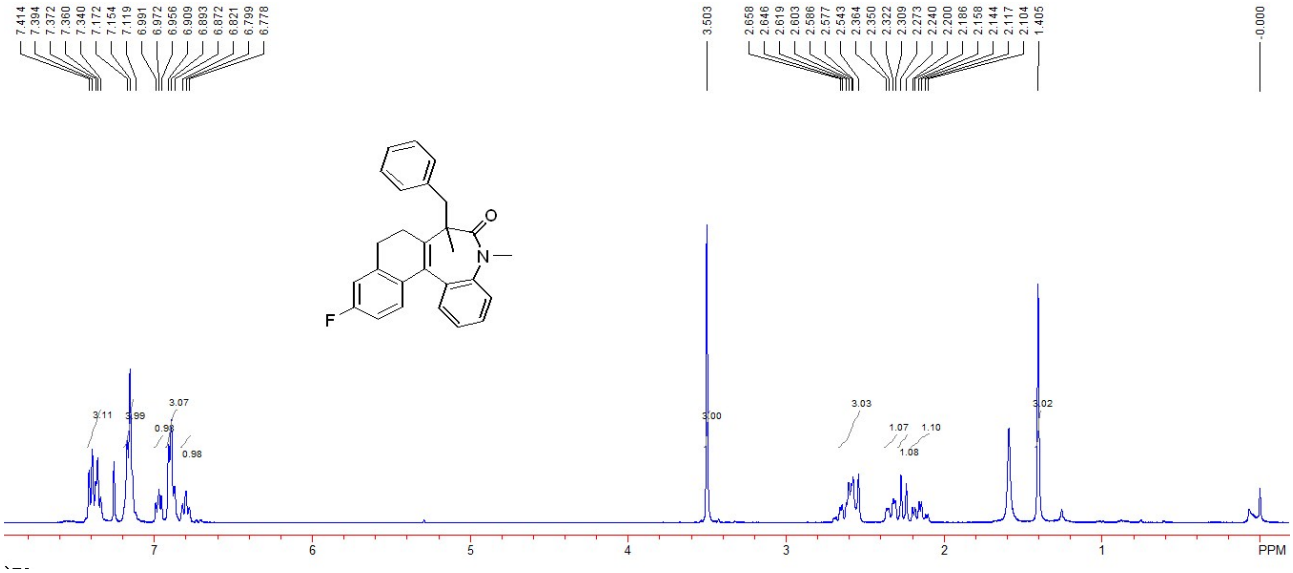


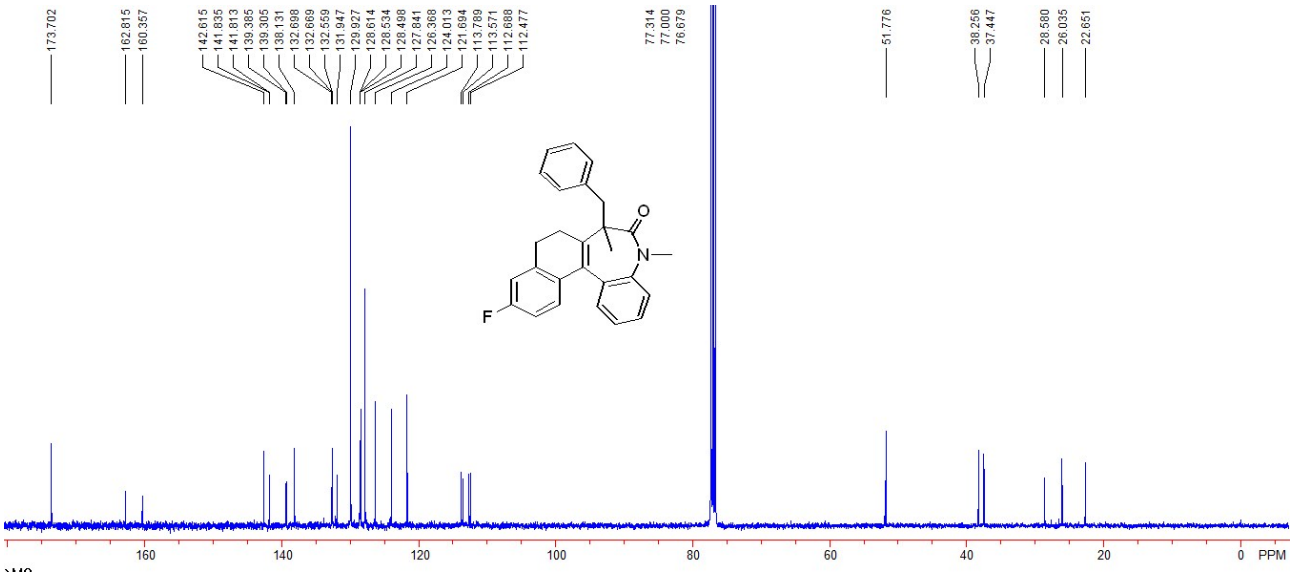


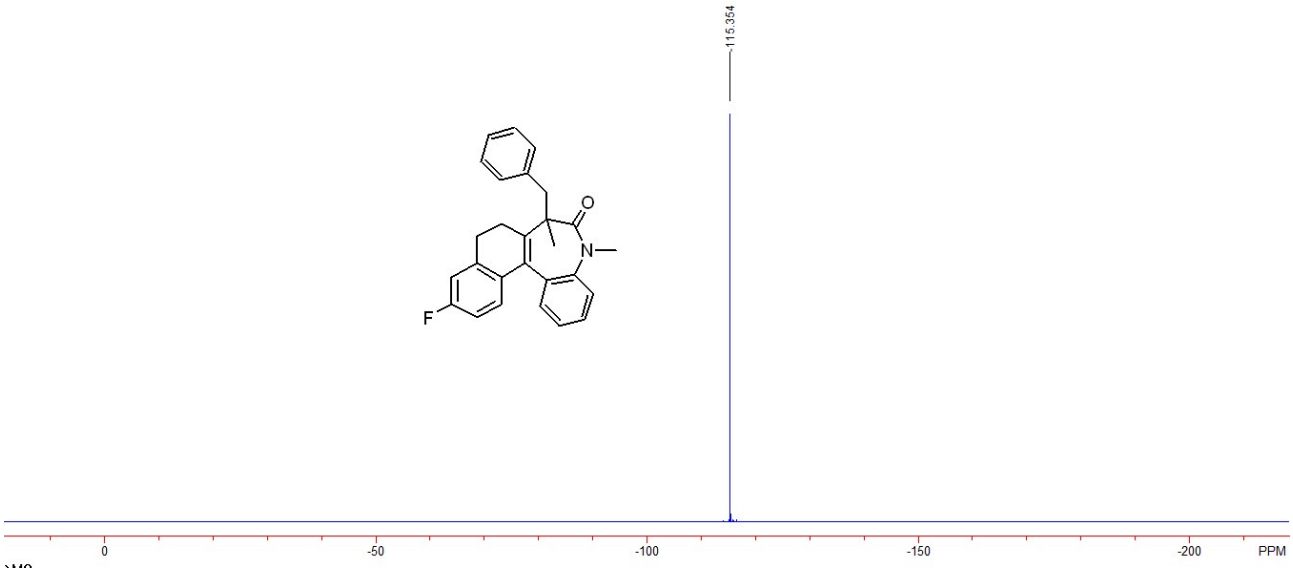


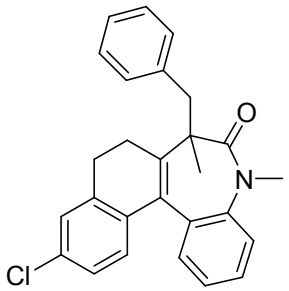
7-Benzyl-11-fluoro-5,7-dimethyl-5,7,8,9-tetrahydro-6*H*-benzo[*b*]naphtho[1,2-*d*]azepin-6-one (3af)

green solid, 54 mg, 68% yield; m. p. 230 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.41-7.34 (m, 3H), 7.17-7.12 (m, 4H), 6.99-6.96 (m, 1H), 6.91-6.87 (m, 3H), 6.80 (t, J = 8.4 Hz, 1H), 3.50 (s, 3H), 2.66-2.54 (m, 3H), 2.34 (dd, J_1 = 5.6 Hz, J_2 = 16.8 Hz, 1H), 2.26 (d, J = 13.2 Hz, 1H), 2.15 (td, J_1 = 5.6 Hz, J_2 = 16.8 Hz, 1H), 1.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 173.7, 161.6 (d, J = 245.8 Hz), 142.6, 141.8, 141.8, 139.4 (d, J = 8.0 Hz), 138.1, 132.7 (d, J = 2.9 Hz), 132.6, 131.9, 129.9, 128.6 (d, J = 8.0 Hz), 128.5, 127.8, 126.4, 124.0, 121.7, 113.7 (d, J = 21.8 Hz), 112.6 (d, J = 21.1 Hz), 51.8, 38.3, 37.4, 28.6, 26.0, 22.7; ^{19}F NMR (376 MHz, $CDCl_3$): δ -115.4; IR (CH_2Cl_2): ν 2988, 2920, 1642, 1595, 1492, 1446, 1349, 1255, 1242, 1090, 1066, 1050, 876, 820, 772, 762, 724, 706, 675, 668 cm^{-1}; HRMS (ESI) Calcd. For $C_{27}H_{25}FNO$ $(M+H)^+$ requires: 398.1915, Found: 398.1913.





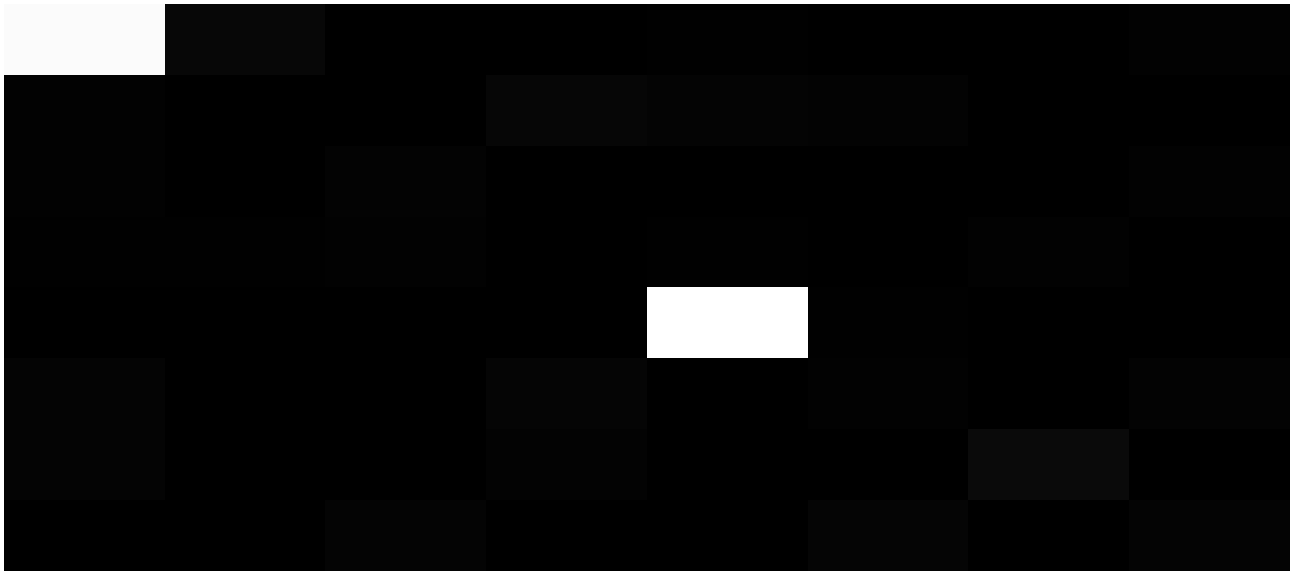


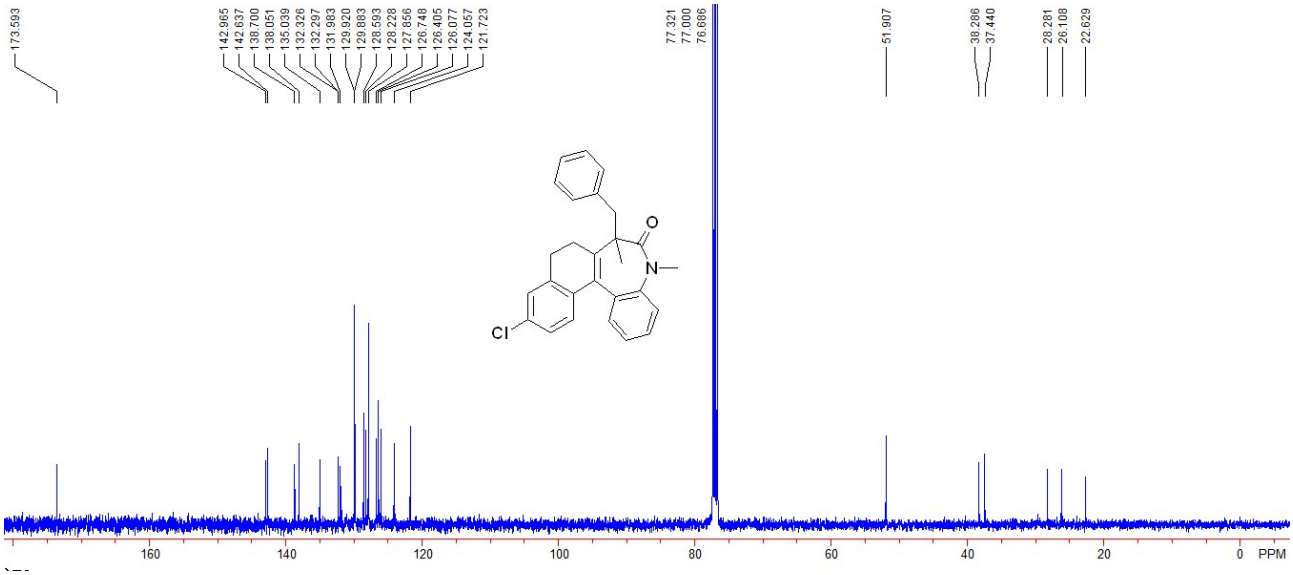


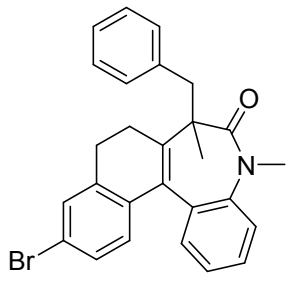
7-Benzyl-11-chloro-5,7-dimethyl-5,7,8,9-tetrahydro-6*H*-benzo[*b*]naphtho[1,2-*d*]azepin-6-one (3ag)

pale green solid, 59 mg, 71% yield; m. p. 201 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.42-7.35 (m, 3H), 7.20-7.13 (m, 5H), 7.11-7.08 (m, 1H), 6.94 (d, J = 8.0 Hz, 1H), 6.91-6.89 (m, 2H), 3.51 (s, 3H), 2.64-2.55 (m, 3H), 2.37-2.31 (m, 1H), 2.26 (d, J = 13.2 Hz, 1H), 2.15 (td, J_1 = 6.4 Hz, J_2 =

16.0 Hz, 1H), 1.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 173.6, 143.0, 142.6, 138.7, 138.1, 135.0, 132.33, 132.30, 132.0, 129.92, 129.88, 128.6, 128.2, 127.9, 126.7, 126.4, 126.1, 124.1, 121.7, 51.9, 38.3, 37.4, 28.3, 26.1, 22.6; IR (CH_2Cl_2): ν 2958, 2922, 1644, 1596, 1579, 1492, 1445, 1350, 1299, 1254, 1241, 1090, 1050, 874, 820, 762, 723, 703, 675, 668 cm^{-1}; HRMS (ESI) Calcd. For $C_{27}H_{25}ClNO$ $(M+H)^+$ requires: 414.1619, Found: 414.1615.



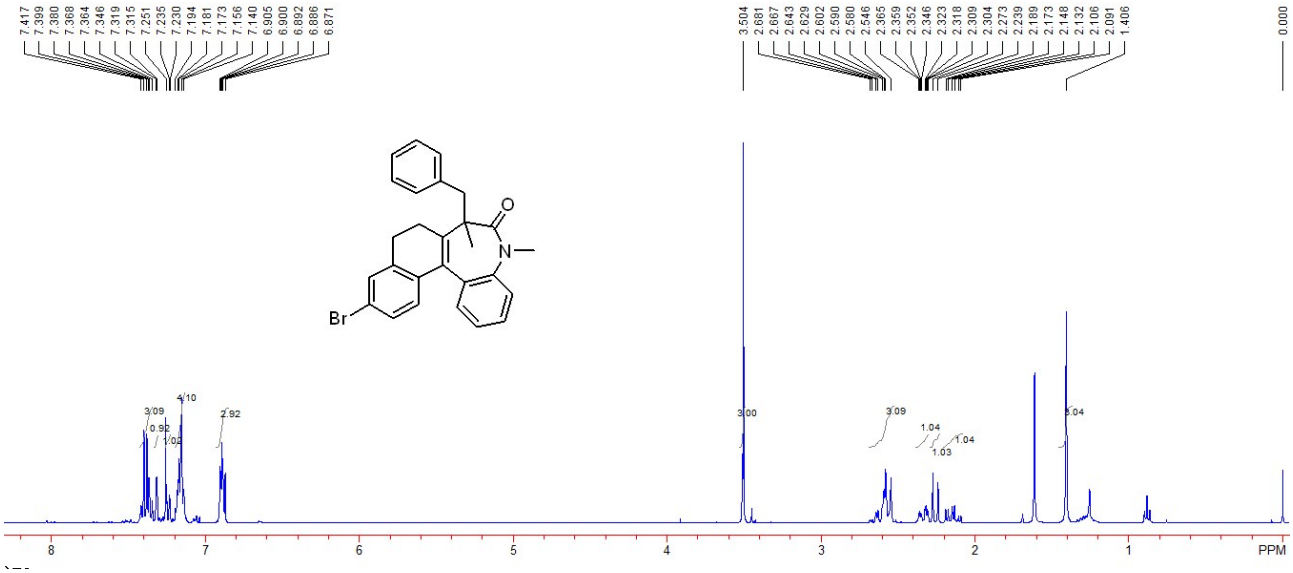


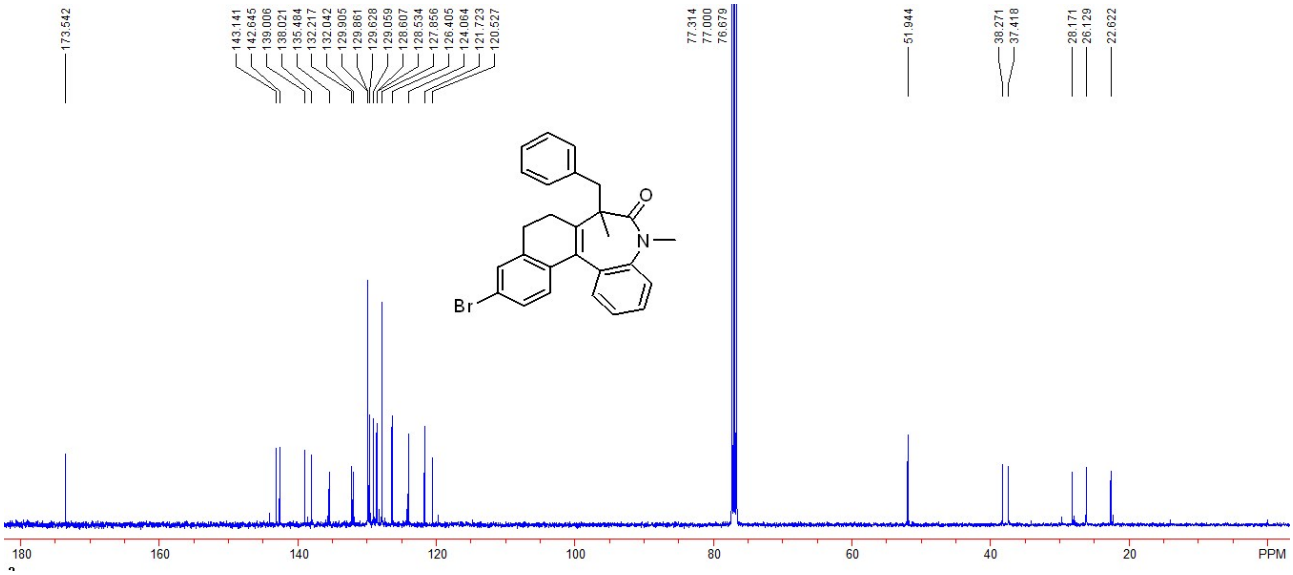


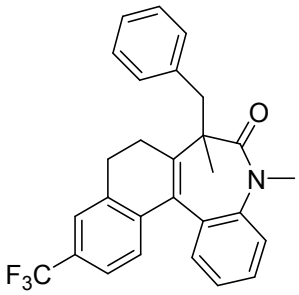
7-Benzyl-11-bromo-5,7-dimethyl-5,7,8,9-tetrahydro-6*H*-benzo[*b*]naphtho[1,2-*d*]azepin-6-one

(3ah)

pale green solid, 67 mg, 73% yield; m. p. 189 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.42-7.35 (m, 3H), 7.32 (d, J = 1.6 Hz, 1H), 7.25-7.23 (m, 1H), 7.19-7.14 (m, 4H), 6.91-6.87 (m, 3H), 3.50 (s, 3H), 2.68-2.55 (m, 3H), 2.37-2.30 (m, 1H), 2.26 (d, J = 13.6 Hz, 1H), 2.14 (td, J_1 = 6.4 Hz, J_2 = 16.4 Hz, 1H), 1.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 173.5, 143.1, 142.6, 139.0, 138.0, 135.5, 132.2, 132.0, 129.91, 129.86, 129.6, 129.1, 128.6, 128.5, 127.9, 126.4, 124.1, 121.7, 120.5, 51.9, 38.3, 37.4, 28.2, 26.1, 22.6; IR (CH_2Cl_2): ν 2923, 2838, 1644, 1596, 1580, 1492, 1479, 1446, 1383, 1379, 1350, 1299, 1255, 1241, 1167, 1160, 1141, 1094, 1090, 1050, 875, 820, 801, 762, 736, 723, 666 cm^{-1}; HRMS (ESI) Calcd. For $C_{27}H_{25}BrNO$ $(M+H)^+$ requires: 458.1114, Found: 458.1107.

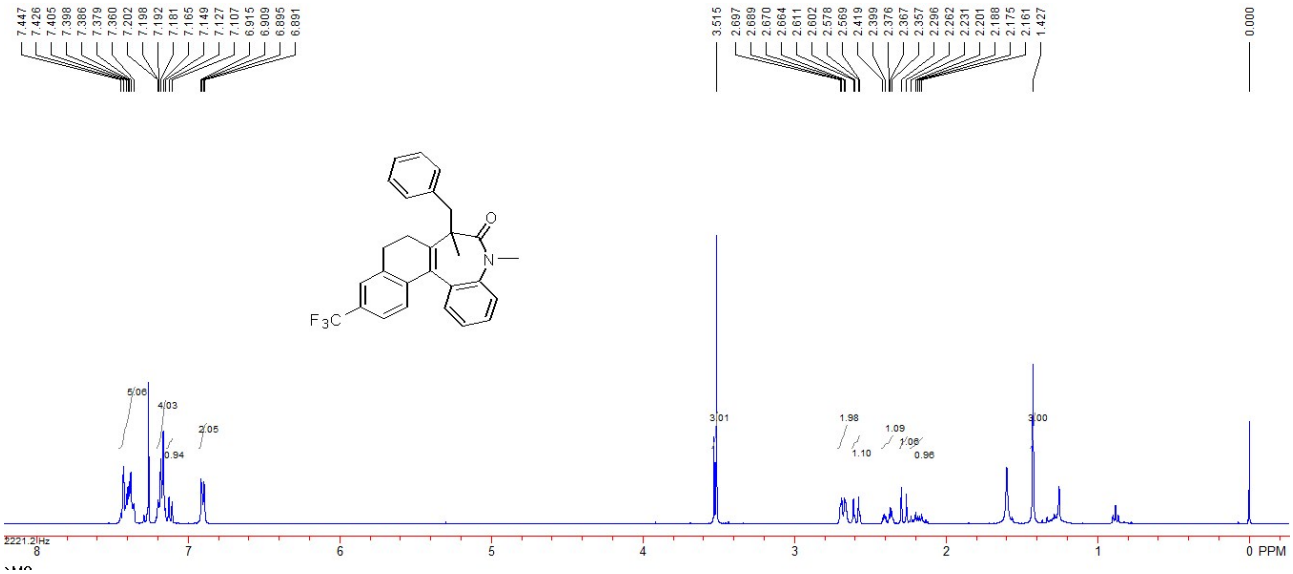


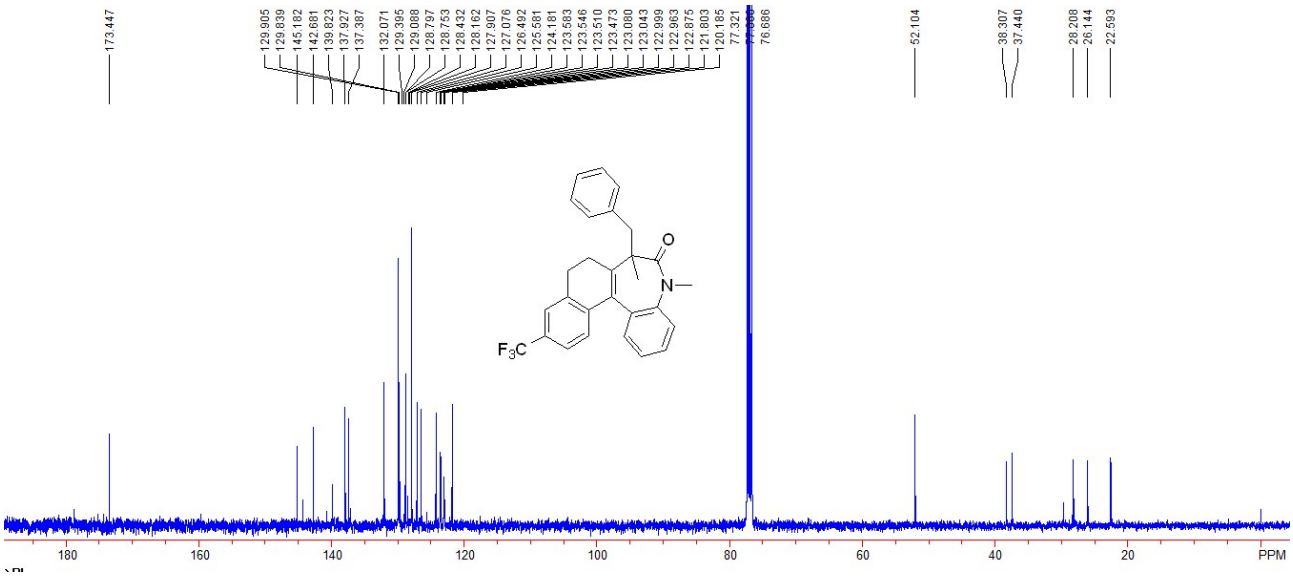


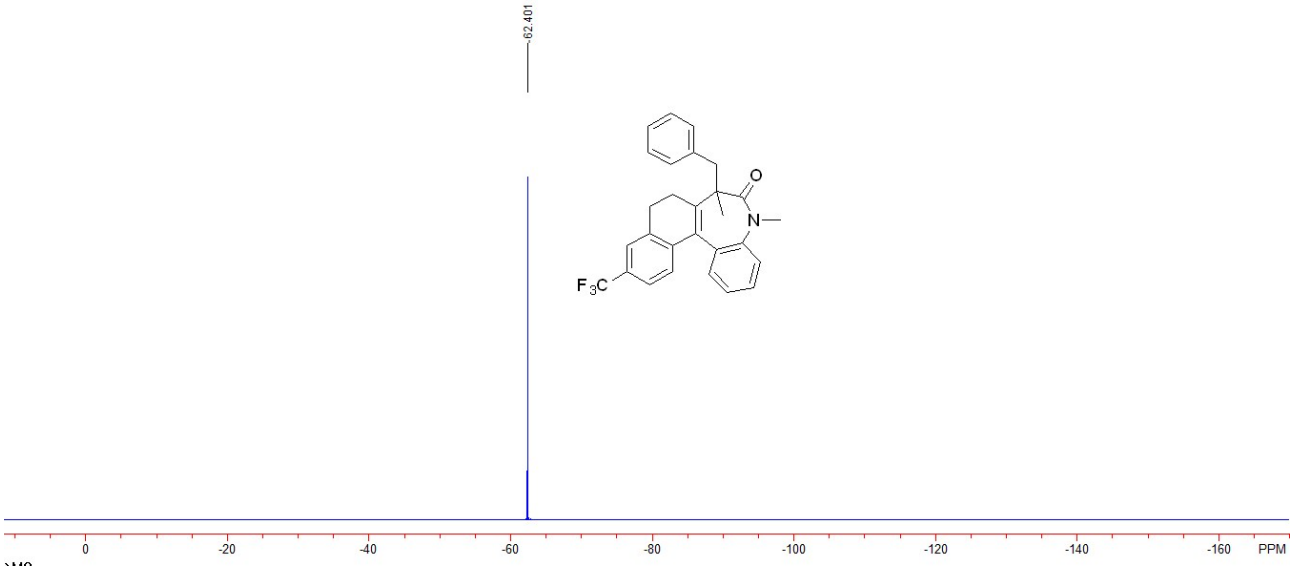


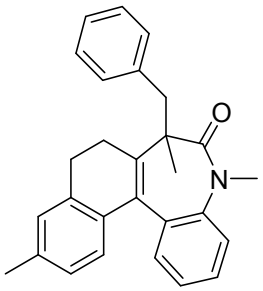
7-Benzyl-5,7-dimethyl-11-(trifluoromethyl)-5,7,8,9-tetrahydro-6*H*-benzo[*b*]naphtho[1,2-*d*]azepin-6-one (3ai)

pale green solid, 56 mg, 62% yield; m. p. 198 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.45-7.36 (m, 5H), 7.20-7.15 (m, 4H), 7.12 (d, J = 8.0 Hz, 1H), 6.92-6.89 (m, 2H), 3.52 (s, 3H), 2.70-2.66 (m, 2H), 2.59 (dd, J_1 = 3.6 Hz, J_2 = 13.2 Hz, 1H), 2.42-2.36 (m, 1H), 2.28 (d, J = 13.6 Hz, 1H), 2.23-2.16 (m, 1H), 1.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 173.4, 145.2, 142.7, 139.8, 137.9, 137.4, 132.1, 129.9, 129.8, 128.9 (q, J = 31.7 Hz), 128.2, 127.9, 127.1, 126.5, 124.3 (q, J = 270.6 Hz), 124.2, 123.5 (q, J = 3.7 Hz), 123.0 (q, J = 3.7 Hz), 121.8, 52.1, 38.3, 37.4, 28.2, 26.1, 22.6; IR (CH_2Cl_2): ν 2956, 2918, 1648, 1597, 1494, 1445, 1425, 1354, 1324, 1278, 1257, 1200, 1162, 1118, 1092, 1074, 838, 764, 740, 700, 668, 654 cm^{-1}; HRMS (ESI) Calcd. For $C_{28}H_{25}F_3NO$ $(M+H)^+$ requires: 448.1883, Found: 448.1877.





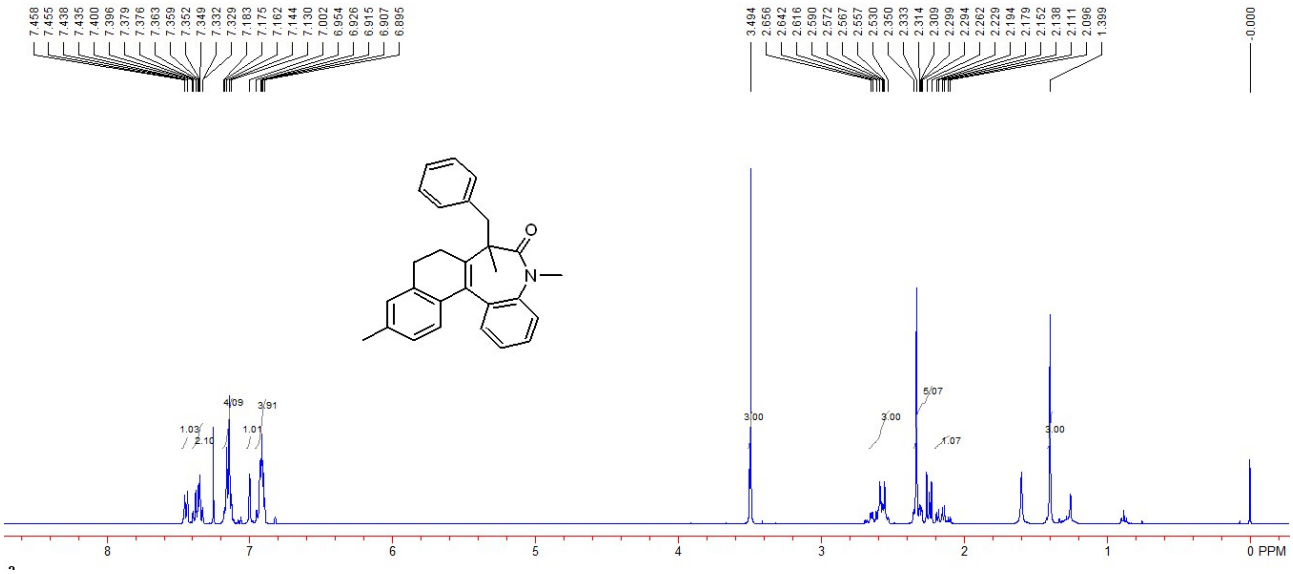


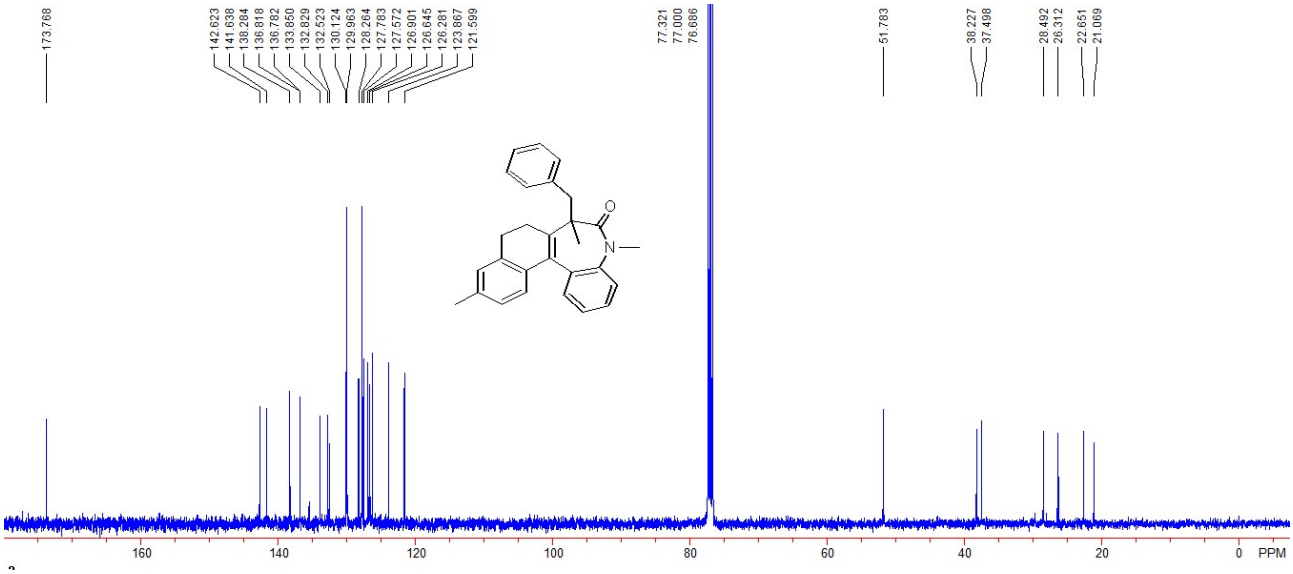


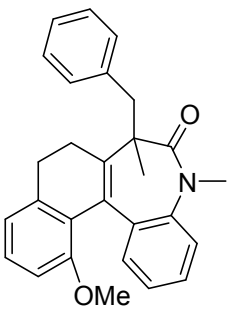
7-Benzyl-5,7,11-trimethyl-5,7,8,9-tetrahydro-6*H*-benzo[*b*]naphtho[1,2-*d*]azepin-6-one (3ak)

green solid, 68 mg, 86% yield; m. p. 210 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.45 (dd, J_1 = 1.2 Hz, J_2 = 8.0 Hz, 1H), 7.40-7.33 (m, 2H), 7.18-7.13 (m, 4H), 7.00 (s, 1H), 6.95-6.90 (m, 4H), 3.49 (s, 3H), 2.66-2.53 (m, 3H), 2.35-2.23 (m, 5H), 2.15 (td, J_1 = 6.0 Hz, J_2 = 16.8 Hz, 1H), 1.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 173.8, 142.6, 141.6, 138.3, 136.82, 136.78, 133.9, 132.8,

132.5, 130.1, 130.0, 128.3, 127.8, 127.6, 126.9, 126.6, 126.3, 123.9, 121.6, 51.8, 38.2, 37.5, 28.5, 26.3, 22.7, 21.1; IR (CH_2Cl_2): ν 2987, 2901, 1645, 1597, 1494, 1446, 1378, 1354, 1257, 1089, 1066, 1050, 822, 764, 719, 699, 668 cm^{-1}; HRMS (ESI) Calcd. For $C_{28}H_{28}NO$ $(M+H)^+$ requires: 394.2165, Found: 394.2158.



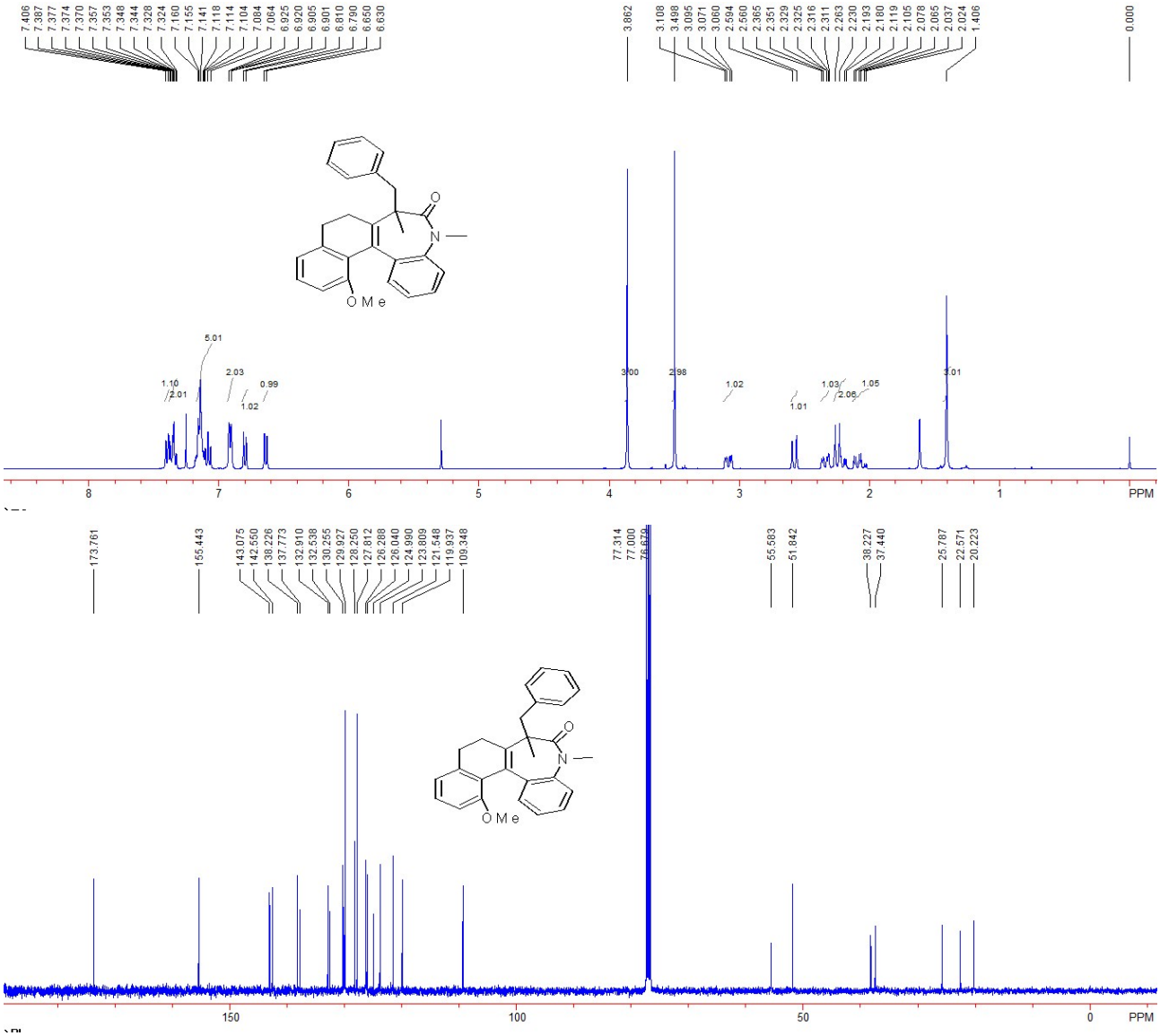


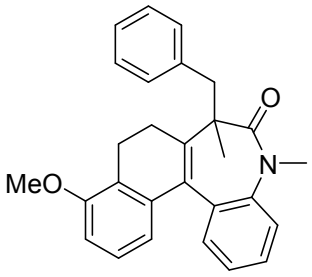


7-Benzyl-13-methoxy-5,7-dimethyl-5,7,8,9-tetrahydro-6*H*-benzo[*b*]naphtho[1,2-*d*]azepin-6-

one(3al)

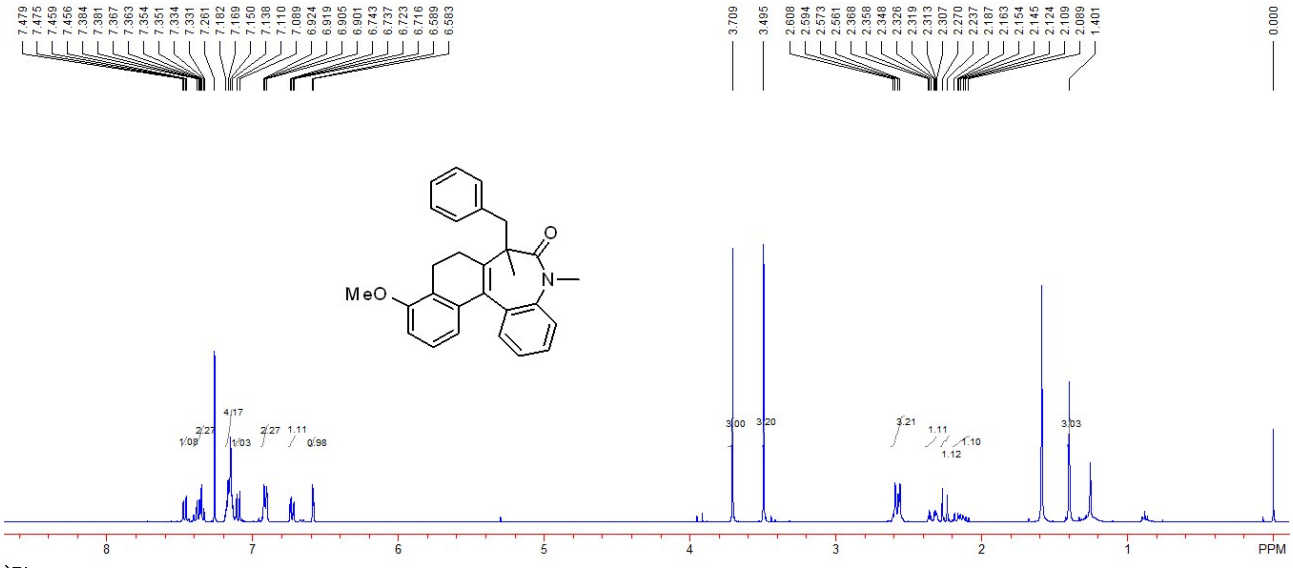
pale green solid, 72 mg, 88% yield; m. p. 231 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.41-7.39 (m, 3H), 7.38-7.34 (m, 2H), 7.17-7.06 (m, 5H), 6.91 (dd, J_1 = 2.0 Hz, J_2 = 8.0 Hz, 2H), 6.80 (d, J = 8.0 Hz, 1H), 6.64 (d, J = 8.0 Hz, 1H), 3.86 (s, 3H), 3.50 (s, 3H), 3.08 (dd, J_1 = 4.0 Hz, J_2 = 15.2 Hz, 1H), 2.58 (d, J = 13.6 Hz, 1H), 2.34 (dd, J_1 = 3.6 Hz, J_2 = 16.0 Hz, 1H), 2.78-2.28 (m, 2H), 2.07 (td, J_1 = 5.2 Hz, J_2 = 16.8 Hz, 1H), 1.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 173.8, 155.4, 143.1, 142.6, 138.2, 137.8, 132.9, 132.5, 130.3, 129.9, 128.3, 127.8, 126.3, 126.0, 125.0, 123.8, 121.6, 119.9, 109.4, 55.6, 51.8, 38.2, 37.4, 25.8, 22.6, 20.2; IR (CH_2Cl_2): ν 2956, 2916, 1632, 1595, 1567, 1494, 1466, 1445, 1436, 1411, 1376, 1357, 1317, 1264, 1227, 1124, 1080, 1068, 1053, 828, 785, 778, 768, 750, 719, 703, 668 cm^{-1}; HRMS (ESI) Calcd. For $C_{28}H_{28}NO_2$ $(M+H)^+$ requires: 410.2115, Found: 410.2107.

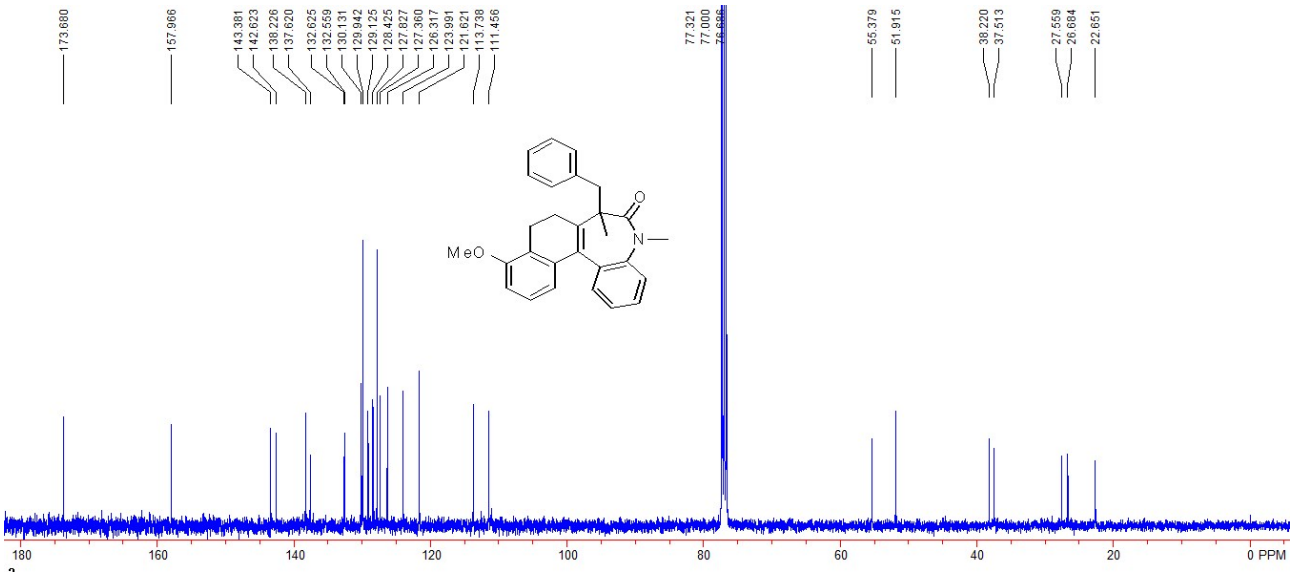


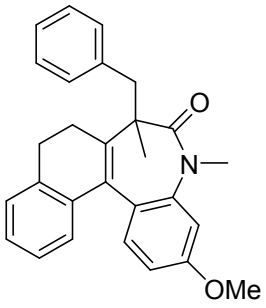


7-Benzyl-10-methoxy-5,7-dimethyl-5,7,8,9-tetrahydro-6*H*-benzo[*b*]naphtho[1,2-*d*]azepin-6-one (3am)

green solid, 71 mg, 87% yield; m. p. 199 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.47 (dd, J_1 = 1.2 Hz, J_2= 7.6 Hz, 1H), 7.38-7.33 (m, 2H), 7.18-7.14 (m, 4H), 7.10 (d, J = 8.4 Hz, 1H), 6.91 (dd, J_1 = 1.6 Hz, J_2 = 7.2 Hz, 2H), 6.73 (dd, J_1 = 2.4 Hz, J_2 = 8.0 Hz, 1H), 6.59 (d, J = 2.4 Hz, 1H), 3.71 (s, 3H), 3.50 (s, 3H), 2.61-2.56 (m, 3H), 2.37-2.31 (m, 1H), 2.25 (d, J = 13.2 Hz, 1H), 2.18-2.09 (m, 1H), 1.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 173.7, 158.0, 143.4, 142.6, 138.2, 137.6, 132.63, 132.56, 130.1, 129.9, 129.1, 128.4, 127.8, 127.4, 126.3, 124.0, 121.6, 113.7, 111.5, 55.4, 51.9, 38.2, 37.5, 27.6, 26.7, 22.7; IR (CH_2Cl_2): ν 2920, 2851, 1645, 1597, 1576, 1493, 1444, 1417, 1352, 1307, 1231, 1209, 1041, 765, 729, 700, 678, 668 cm^{-1}; HRMS (ESI) Calcd. For $C_{28}H_{28}NO_2$ $(M+H)^+$ requires: 410.2115, Found: 410.2109.

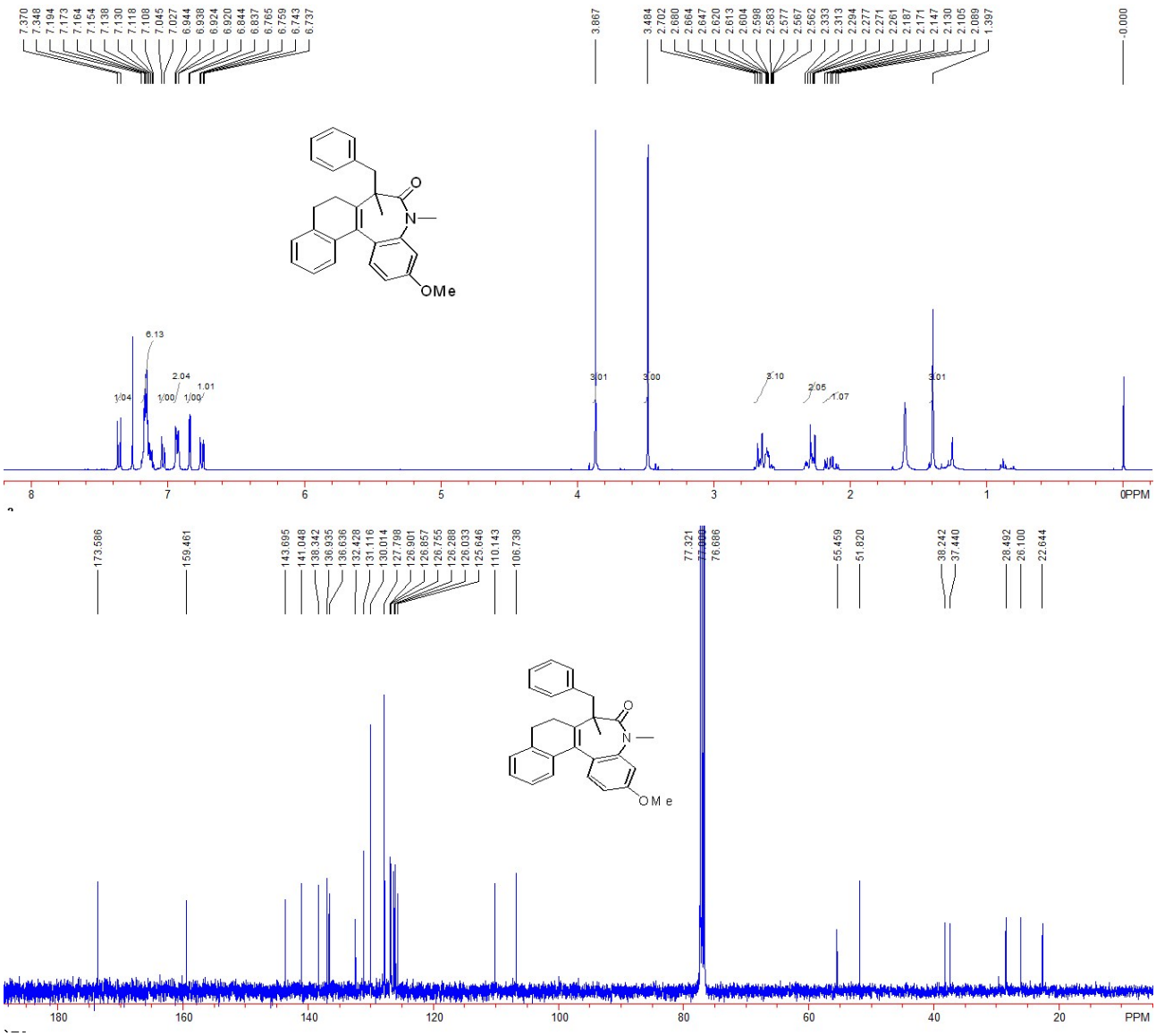


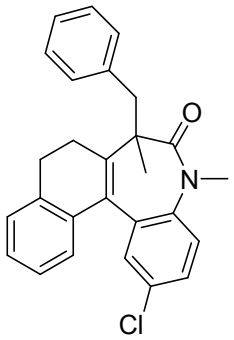




7-Benzyl-3-methoxy-5,7-dimethyl-5,7,8,9-tetrahydro-6*H*-benzo[*b*]naphtho[1,2-*d*]azepin-6-one (3an)

pale green solid, 70 mg, 84% yield; m. p. 219 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.36 (d, J = 8.8 Hz, 1H), 7.19-7.11 (m, 6H), 7.04 (d, J = 7.2 Hz, 1H), 6.94-6.92 (m, 2H), 6.84 (d, J = 2.8 Hz, 1H), 6.75 (dd, J_1 = 2.4 Hz, J_2 = 8.8 Hz, 1H), 3.87 (s, 3H), 3.48 (s, 3H), 2.70-2.56 (m, 3H), 2.33-2.26 (m, 2H), 2.14 (td, J_1 = 6.4 Hz, J_2 = 16.0 Hz, 1H), 1.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 173.6, 159.5, 143.7, 141.0, 138.3, 136.9, 136.6, 132.4, 131.1, 130.0, 127.8, 126.90, 126.86, 126.76, 126.3, 126.0, 125.6, 110.1, 106.7, 55.5, 51.8, 38.2, 37.4, 28.5, 26.1, 22.6; IR (CH_2Cl_2): ν 2956, 2919, 1643, 1603, 1495, 1464, 1332, 1229, 1186, 1081, 1032, 1020, 966, 894, 815, 769, 743, 698, 668 cm^{-1}; HRMS (ESI) Calcd. For $C_{28}H_{28}NO_2$ $(M+H)^+$ requires: 410.2115, Found: 410.2114.

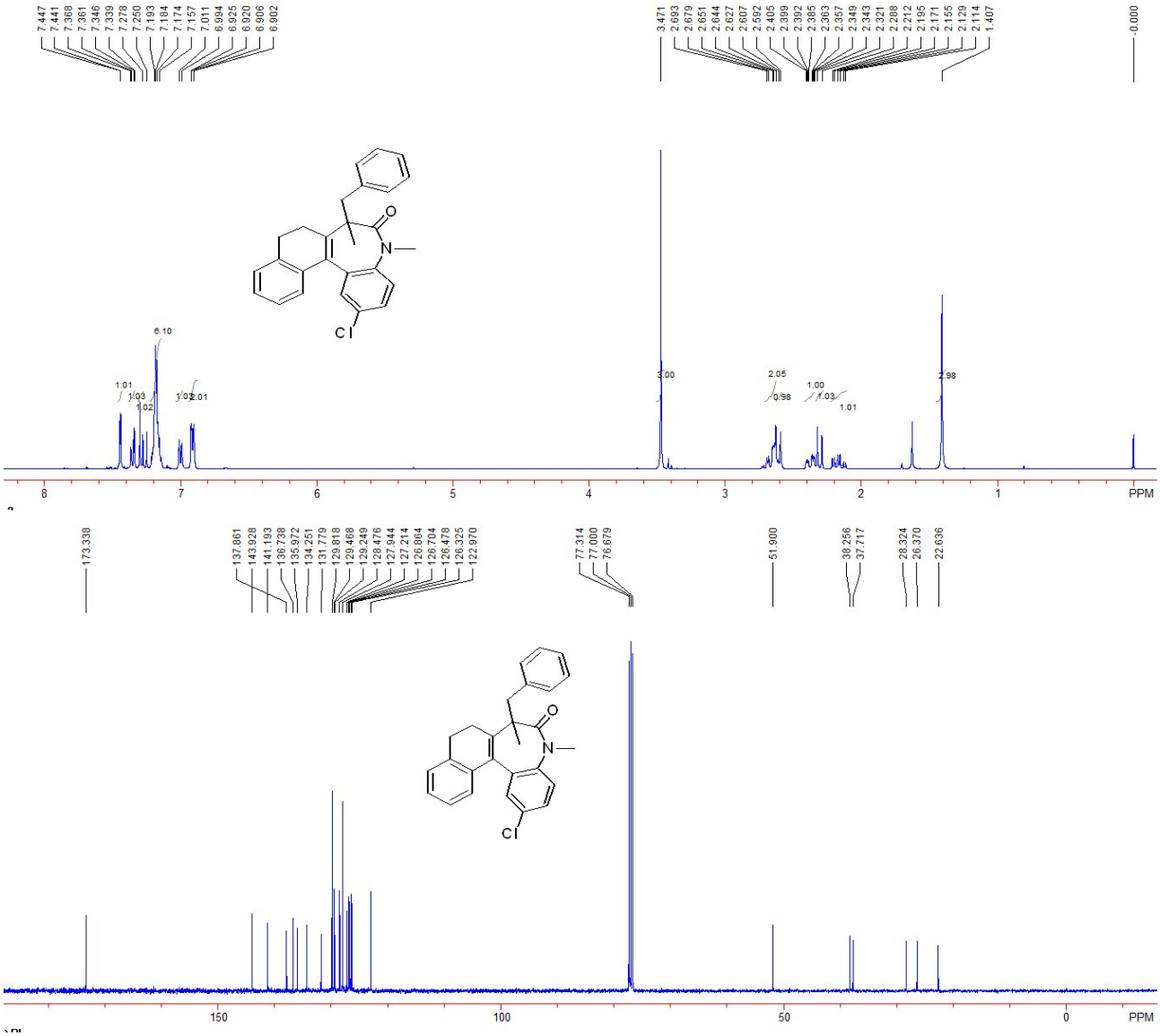


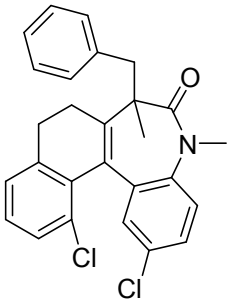


7-Benzyl-2-chloro-5,7-dimethyl-5,7,8,9-tetrahydro-6*H*-benzo[*b*]naphtho[1,2-*d*]azepin-6-one (3ao)

pale green solid, 65 mg, 78% yield; m. p. 229 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.44 (d, J = 2.4 Hz, 1H), 7.35 (dd, J_1 = 2.8 Hz, J_2 = 8.8 Hz, 1H), 7.29 (d, J = 8.8 Hz, 1H), 7.19-7.16 (m, 6H), 7.00 (d, J = 6.8 Hz, 1H), 6.91 (dd, J_1 = 2.0 Hz, J_2 = 7.2 Hz, 2H), 3.47 (s, 3H), 2.69-2.64 (m, 2H),

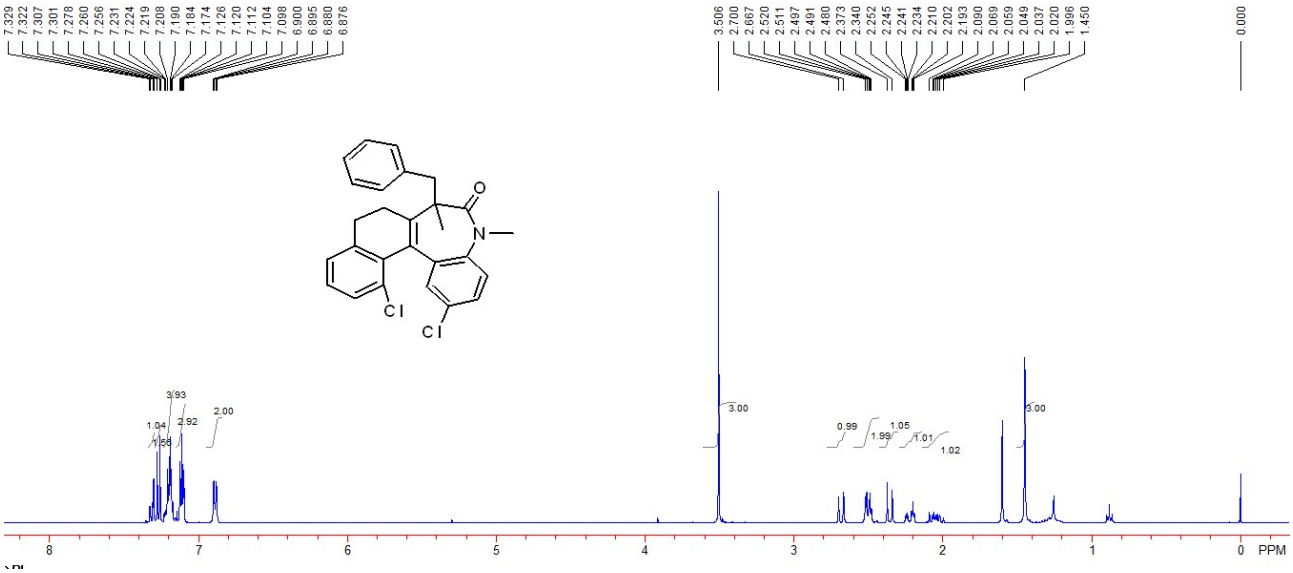
2.63-2.59 (m, 1H), 2.37 (ddd, J_1 = 2.4 Hz, J_2 = 5.2 Hz, J_3 = 16.8 Hz, 1H), 2.30 (d, J = 13.2 Hz, 1H), 2.16 (td, J_1 = 6.8 Hz, J_2 = 16.4 Hz, 1H), 1.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 173.3, 143.9, 141.2, 137.9, 136.7, 136.0, 134.3, 131.8, 129.8, 129.5, 129.2, 128.5, 127.9, 127.2, 126.9, 126.7, 126.5, 126.3, 123.0, 51.9, 38.3, 37.7, 28.3, 26.4, 22.6; IR (CH_2Cl_2): ν 2945, 2922, 1638, 1485, 1466, 1453, 1400, 1382, 1344, 1298, 1251, 1105, 1090, 829, 770, 746, 727, 710, 683, 657 cm^{-1}; HRMS (ESI) Calcd. For $C_{27}H_{25}ClNO$ $(M+H)^+$ requires: 414.1619, Found: 414.1615.

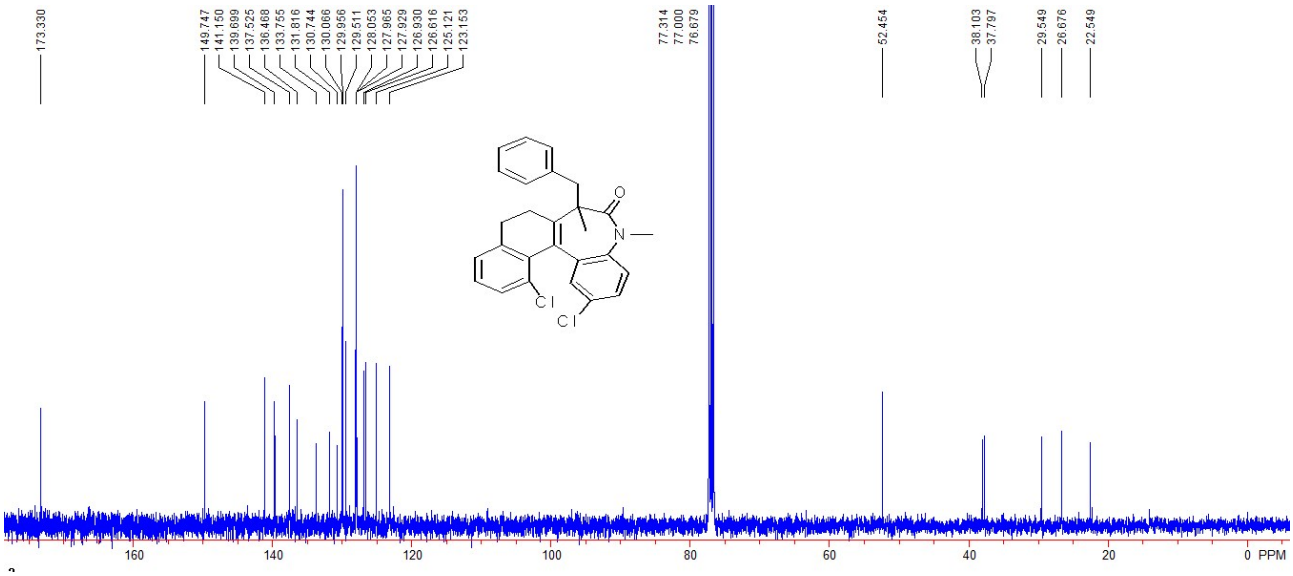


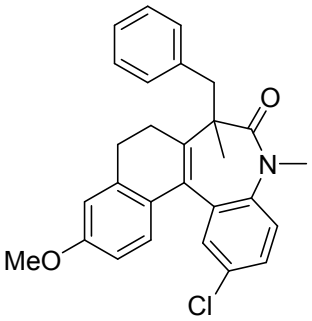


7-Benzyl-2,13-dichloro-5,7-dimethyl-5,7,8,9-tetrahydro-6*H*-benzo[*b*]naphtho[1,2-*d*]azepin-6-one (3ap)

pale green solid, 72 mg, 80% yield; m. p. 183 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.32 (dd, J_1 = 2.8 Hz, J_2 = 8.8 Hz, 1H), 7.27 (d, J = 8.8 Hz, 1H), 7.23-7.17 (m, 4H), 7.13-7.10 (m, 3H), 6.89 (dd, J_1 = 2.0 Hz, J_2 = 8.0 Hz, 2H), 3.51 (s, 3H), 2.68 (d, J = 13.2 Hz, 1H), 2.52-2.48 (m, 2H), 2.36 (d, J = 13.2 Hz, 1H), 2.25-2.19 (m, 1H), 2.09-2.00 (m, 1H), 1.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 173.3, 149.7, 141.2, 139.7, 137.5, 136.5, 133.8, 131.8, 130.7, 130.1, 130.0, 129.5, 128.1, 128.0, 127.9, 126.9, 126.6, 125.1, 123.2, 52.5, 38.1, 37.8, 29.5, 26.7, 22.5; IR (CH_2Cl_2): ν 2946, 2920, 1643, 1601, 1500, 1463, 1452, 1321, 1155, 1104, 1034, 853, 789, 738, 706, 683, 669 cm^{-1}; HRMS (ESI) Calcd. For $C_{28}H_{26}Cl_2NO_2$ $(M+H)^+$ requires: 447.1157, Found: 447.1152.

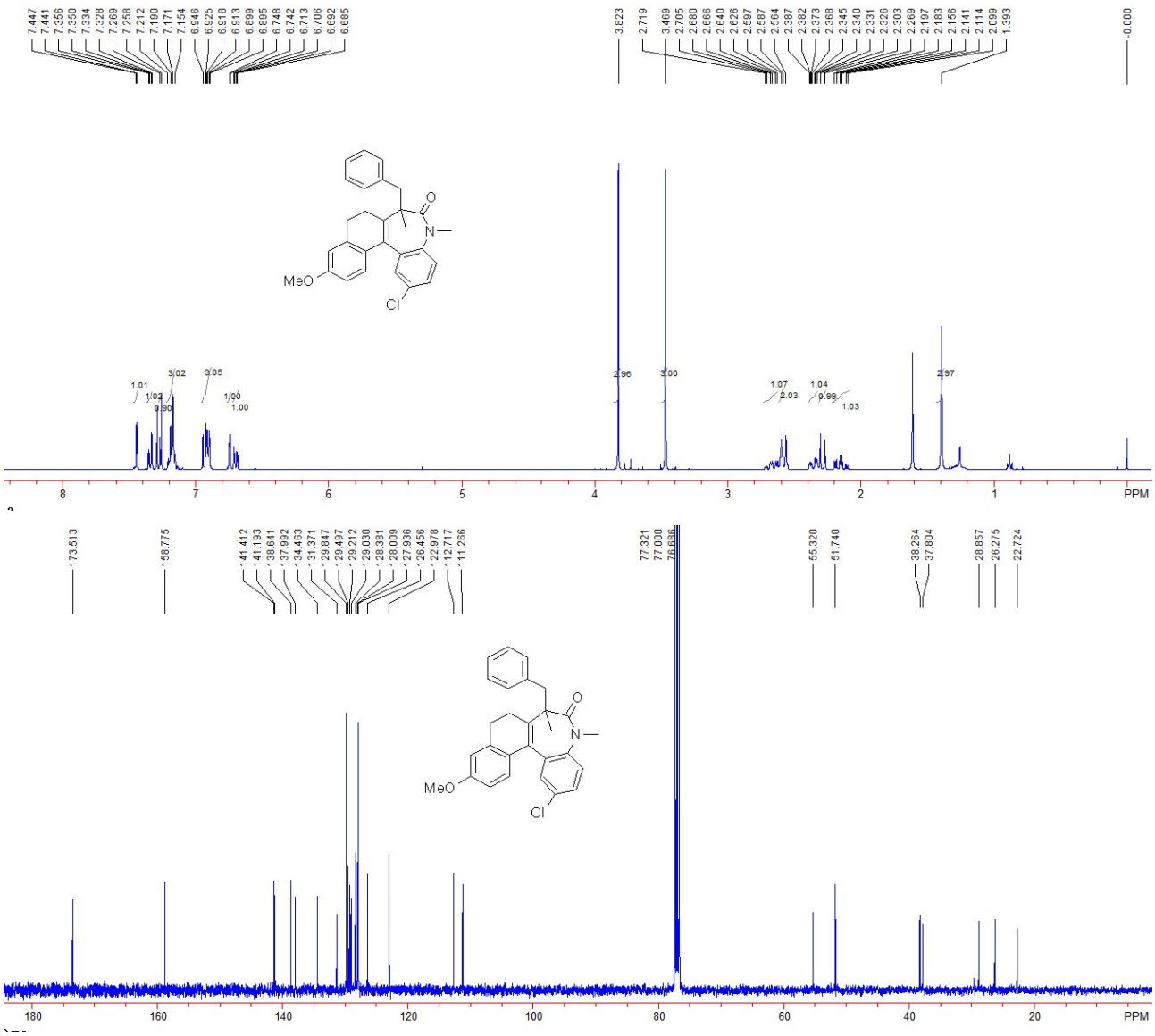


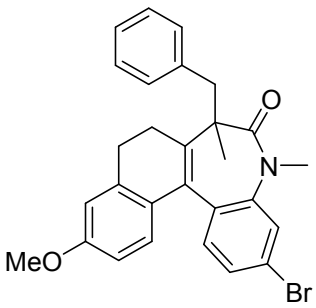




7-Benzyl-2-chloro-11-methoxy-5,7-dimethyl-5,7,8,9-tetrahydro-6*H*-benzo[*b*]naphtho[1,2-*d*]azepin-6-one (3aq)

pale green solid, 76 mg, 86% yield; m. p. 180 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.44 (d, J = 2.4 Hz, 1H), 7.34 (dd, J_1 = 2.4 Hz, J_2 = 8.8 Hz, 1H), 7.26 (d, J = 4.4 Hz, 1H), 6.95-6.90 (m, 3H), 6.75 (d, J = 2.4 Hz, 1H), 6.70 (dd, J_1 = 2.8 Hz, J_2 = 8.4 Hz, 1H), 3.82 (s, 3H), 3.47 (s, 3H), 2.67 (td, J_1 = 5.6 Hz, J_2 = 15.6 Hz, 1H), 2.60-2.56 (m, 2H), 2.36 (ddd, J_1 = 2.0 Hz, J_2 = 5.6 Hz, J_3 = 16.8 Hz, 1H), 2.29 (d, J = 13.6 Hz, 1H), 2.15 (td, J_1 = 6.0 Hz, J_2 = 16.8 Hz, 1H), 1.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 173.5, 158.8, 141.4, 141.2, 138.6, 138.0, 134.5, 131.4, 129.8, 129.5, 129.2, 129.0, 128.4, 128.0, 127.9, 126.5, 123.0, 112.7, 111.3, 55.3, 51.7, 38.3, 37.8, 28.9, 26.3, 22.7; IR (CH_2Cl_2): ν 2945, 2924, 1638, 1607, 1489, 1463, 1452, 1301, 1255, 1104, 1034, 829, 777, 738, 706, 683, 667 cm^{-1}; HRMS (ESI) Calcd. For $C_{28}H_{27}ClNO_2$ $(M+H)^+$ requires: 444.1725, Found: 444.1722.

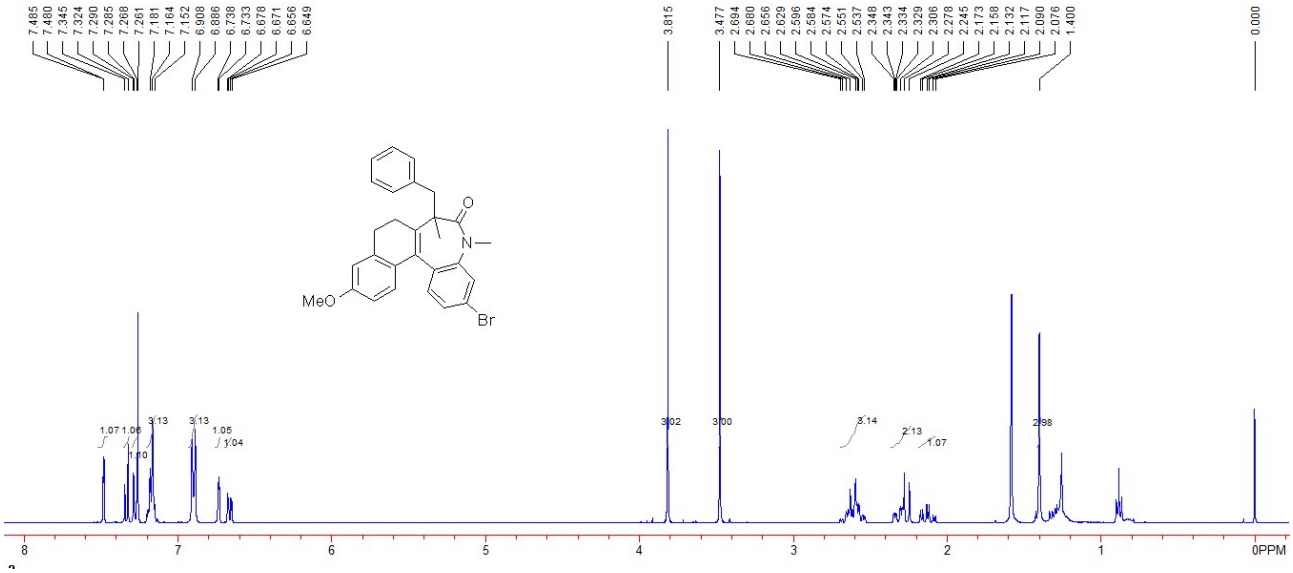


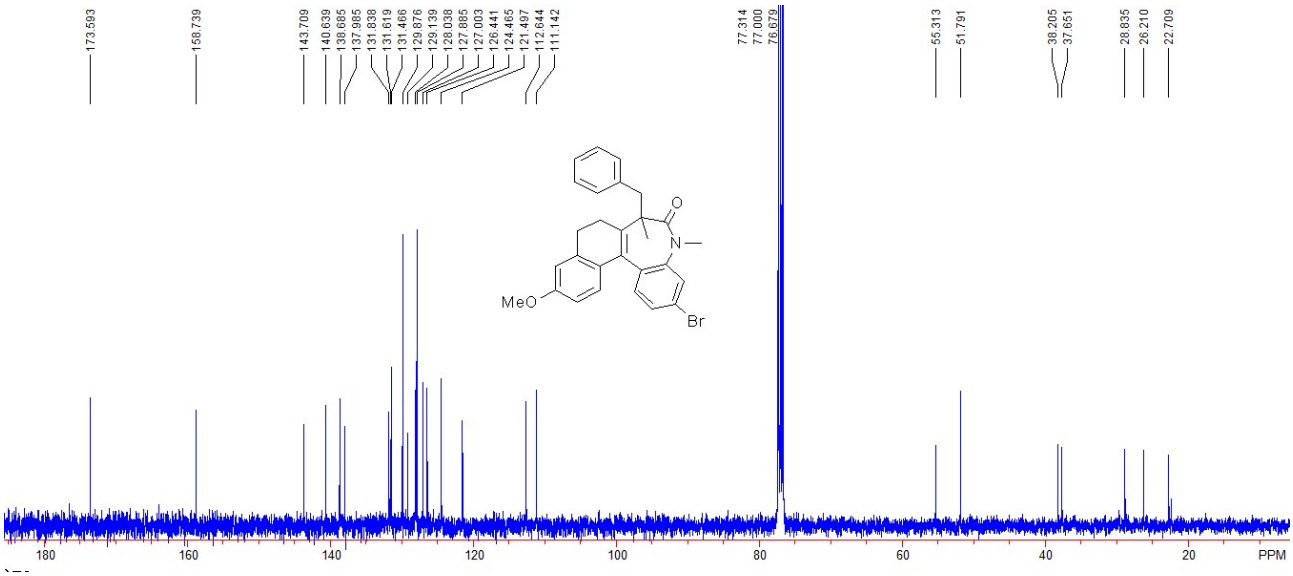


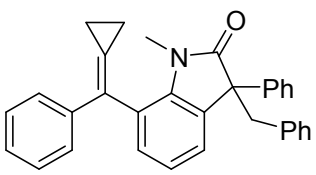
7-Benzyl-3-bromo-11-methoxy-5,7-dimethyl-5,7,8,9-tetrahydro-6*H*-benzo[*b*]naphtho[1,2-*d*]azepin-6-one (3ar)

pale green solid, 85 mg, 87% yield; m. p. 223 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.48 (d, J = 2.0 Hz, 1H), 7.33 (d, J = 8.4 Hz, 1H), 7.29-7.27 (m, 1H), 7.18-7.15 (m, 3H), 6.90 (d, J = 8.8 Hz, 3H), 6.73 (d, J = 2.0 Hz, 1H), 6.66 (dd, J_1 = 2.8 Hz, J_2 = 8.8 Hz, 1H), 3.82 (s, 3H), 3.48 (s, 3H),

2.69-2.54 (m, 3H), 2.35-2.25 (m, 2H), 2.12 (td, J_1 = 6.0 Hz, J_2 = 16.4 Hz, 1H), 1.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 173.6, 158.7, 143.7, 140.6, 138.7, 138.0, 131.8, 131.6, 131.5, 129.9, 129.1, 128.0, 127.9, 127.0, 126.4, 124.5, 121.5, 112.6, 111.1, 55.3, 51.8, 38.2, 37.7, 28.8, 26.2, 22.7; IR (CH_2Cl_2): ν 2958, 2918, 1649, 1602, 1580, 1500, 1487, 1462, 1403, 1307, 1243, 1086, 1034, 1020, 851, 829, 817, 759, 750, 705, 674, 668, 659 cm^{-1}; HRMS (ESI) Calcd. For $C_{28}H_{27}BrNO_2$ $(M+H)^+$ requires: 488.1220, Found: 488.1219.

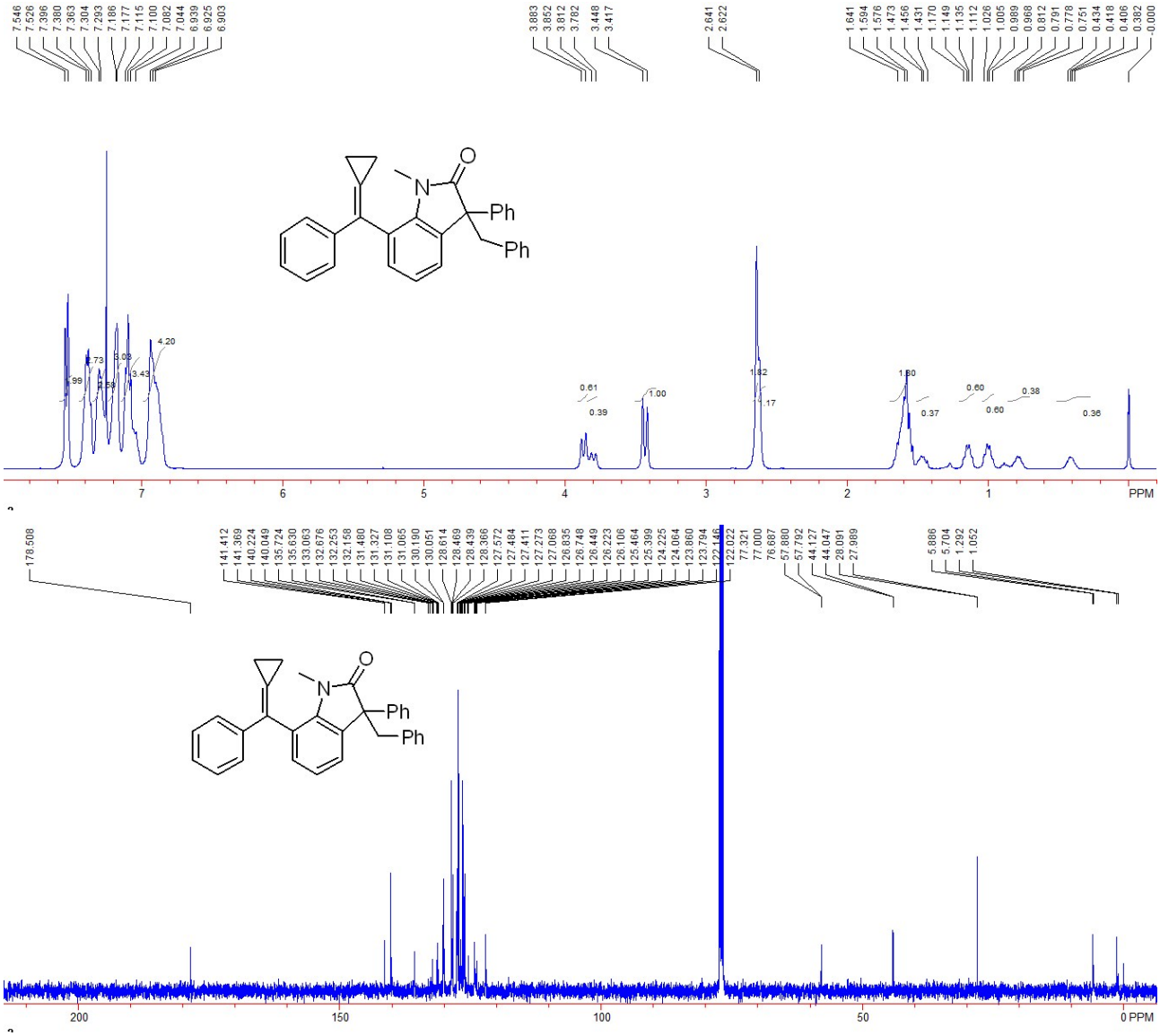


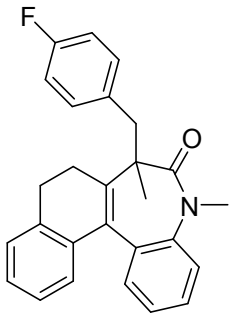




3-Benzyl-7-(cyclopropylidene(phenyl)methyl)-1-methyl-3-phenylindolin-2-one (3as')

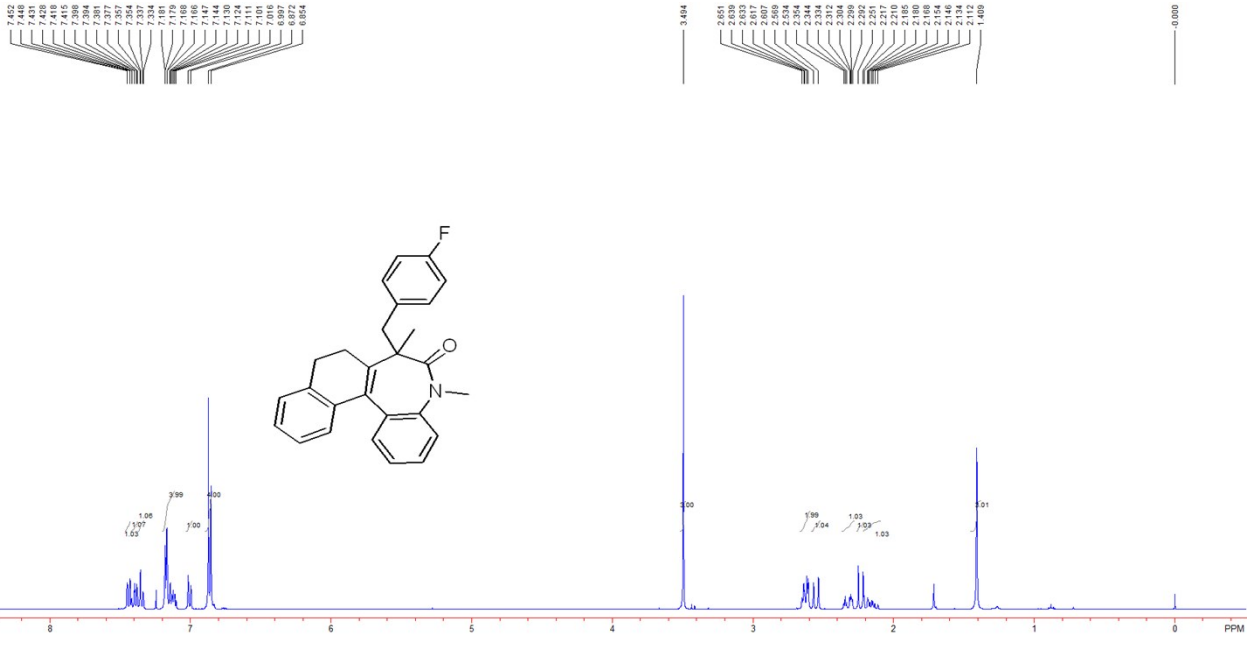
green solid, 71 mg, 80% yield; m. p. 160 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.54 (d, J_1 = 8.0 Hz, 2H), 7.40-7.36 (m, 2.73H), 7.30-7.29 (m, 2.58H), 7.19-7.18 (m, 3H), 7.12-7.04 (m, 3.43H), 6.94-6.90 (m, 4.20H), 3.87 (d, J = 12.4 Hz, 0.61H), 3.80 (d, J = 12.0 Hz, 0.39H), 3.43 (d, J = 12.4 Hz, 1H), 2.64 (s, 1.82H), 2.62 (s, 1.17H), 1.64-1.58 (m, 1.80H), 1.47-1.43 (m, 0.37H), 1.17-1.11 (m, 0.60H), 1.03-0.97 (m, 0.60H), 0.81-0.75 (m, 0.38H), 0.43-0.38 (m, 0.36H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 178.5, 141.41, 141.37, 140.2, 140.0, 135.7, 135.6, 133.1, 132.7, 132.3, 132.2, 131.5, 131.3, 131.1, 131.0, 130.2, 130.1, 128.6, 128.5, 128.44, 128.37, 127.6, 127.5, 127.4, 127.3, 127.1, 126.8, 126.7, 126.4, 126.2, 126.1, 125.5, 125.4, 124.2, 124.1, 123.9, 123.8, 122.1, 122.0, 57.9, 57.8, 44.1, 44.0, 28.1, 28.0, 5.9, 5.7, 1.3, 1.1; IR (CH_2Cl_2): ν 3089, 2941, 2929, 1790, 1680, 1658, 1572, 1450, 1429, 1378, 1369, 1220, 1090, 872, 808, 777, 753, 730, 676, 686, 670 cm^{-1}; HRMS (ESI) Calcd. For $C_{32}H_{28}NO$ $(M+H)^+$ requires: 442.2165, Found: 442.2163.

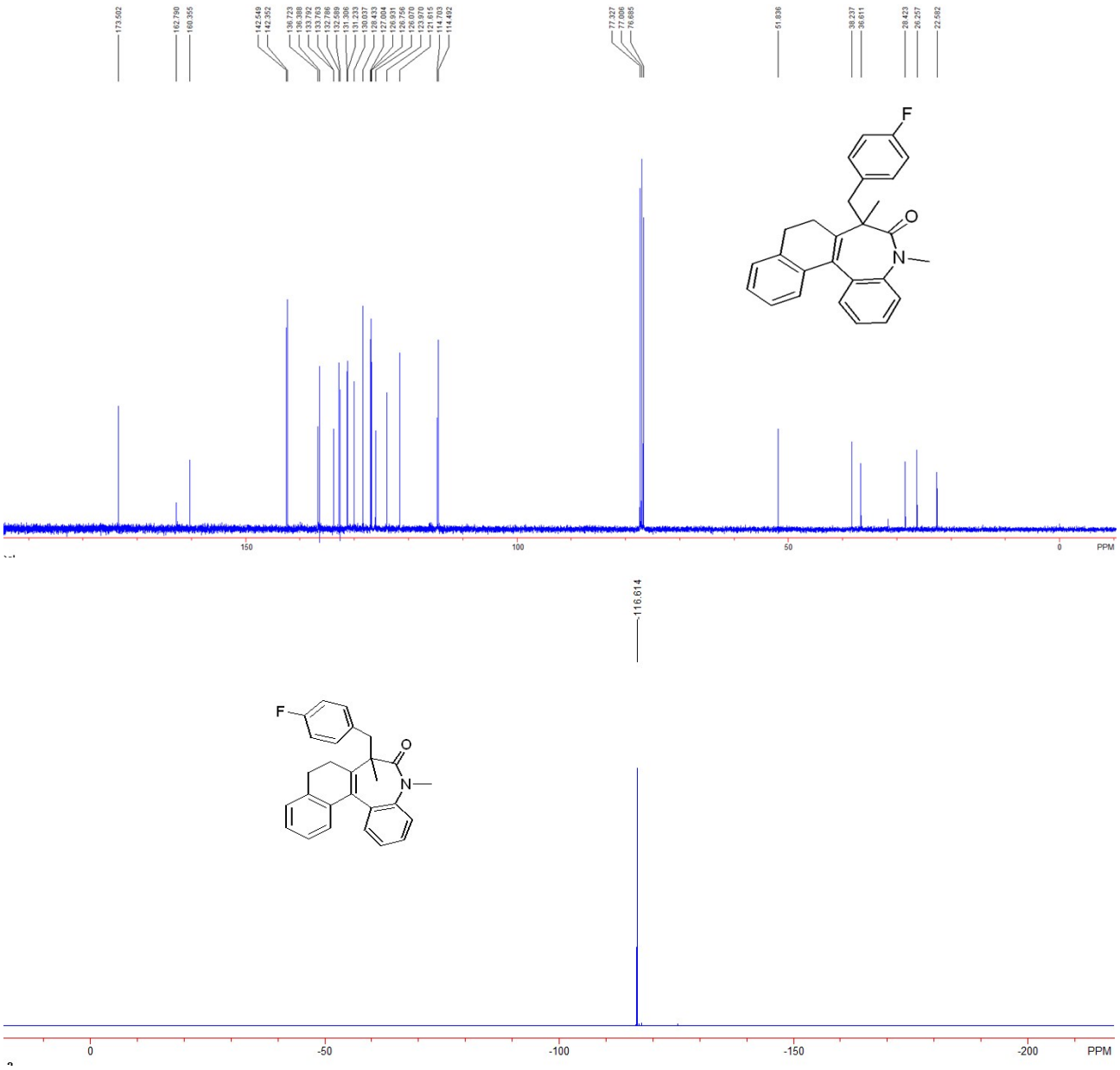


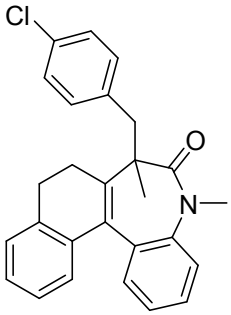


7-(4-fluorobenzyl)-5,7-Dimethyl-5,7,8,9-tetrahydro-6*H*-benzo[*b*]naphtho[1,2-*d*]azepin-6-one (3ba)

green solid, 71 mg, 89% yield; m. p. 211 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.45 (dd, J_1 = 1.6 Hz, J_2 = 8.4 Hz, 1H), 7.42-7.38 (m, 1H), 7.35 (dd, J_1 = 1.2 Hz, J_2 = 8.0 Hz, 1H), 7.18-7.15 (m, 3H), 7.14-7.10 (m, 1H), 7.01 (d, J = 7.6 Hz, 1H), 6.86 (d, J = 7.2 Hz, 4H), 3.49 (s, 3H), 2.65-2.61 (m, 2H), 2.55 (d, J = 14.0 Hz, 1H), 2.35-2.29 (m, 1H), 2.23 (d, J = 13.6 Hz, 1H), 2.21-2.13 (m, 1H), 1.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 173.5, 161.6 (d, J = 243.6 Hz), 142.6, 142.4, 136.7, 136.4, 133.8, 132.8, 132.6, 131.3 (d, J = 7.4 Hz), 130.0, 128.4, 127.0, 126.9, 126.8, 126.1, 124.0, 121.6, 114.6 (d, J = 21.2 Hz), 51.8, 38.2, 36.6, 28.4, 26.2, 22.6; ^{19}F NMR (376 MHz, $CDCl_3$): δ -116.6; IR (CH_2Cl_2): ν 2921, 2910, 1648, 1595, 1490, 1443, 1378, 1356, 1230, 1090, 1014, 851, 808, 777, 763, 753, 730, 676, 666, 655 cm^{-1}; HRMS (ESI) Calcd. For $C_{27}H_{25}FNO$ $(M+H)^+$ requires: 398.1915, Found: 398.1910.



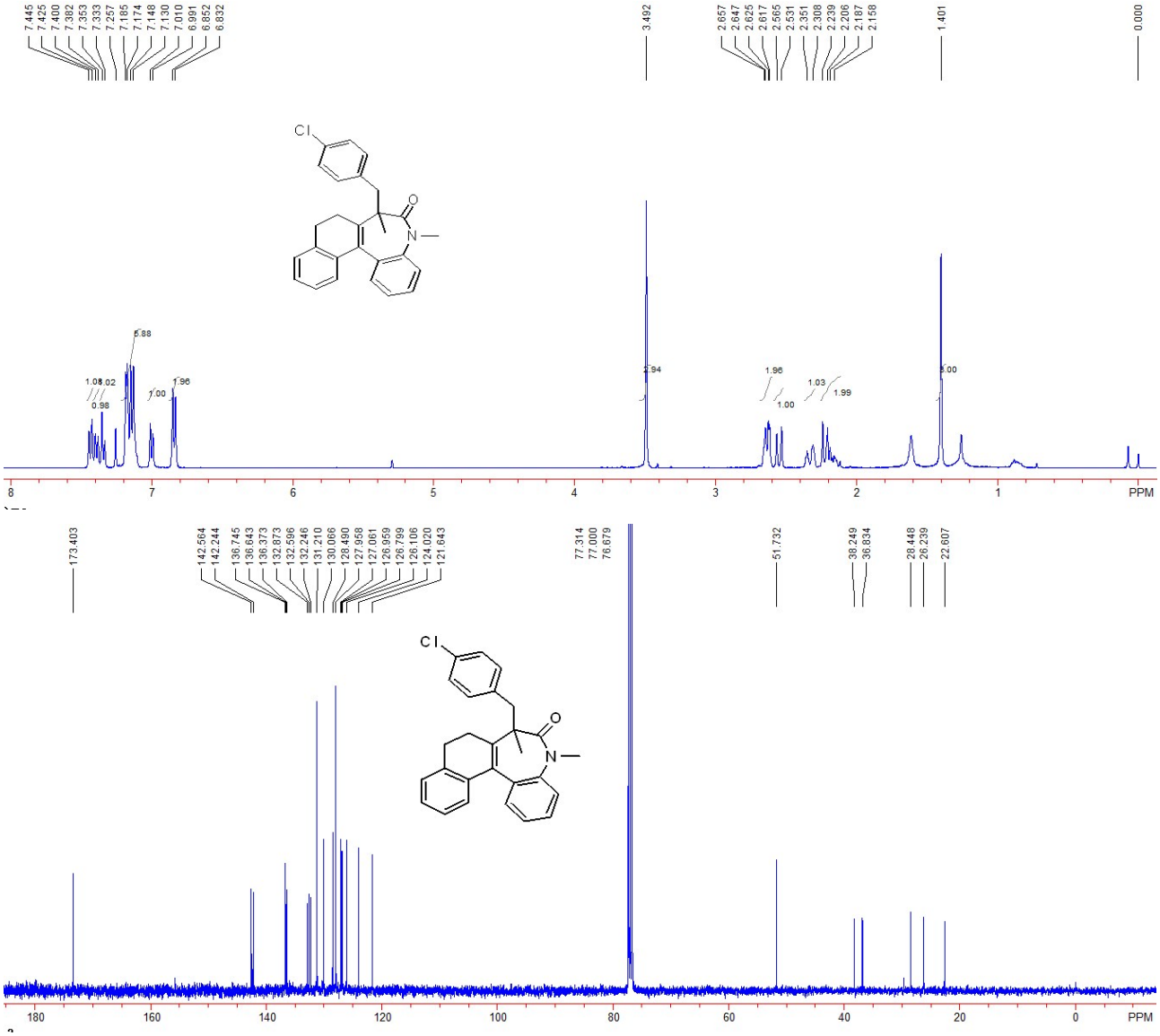


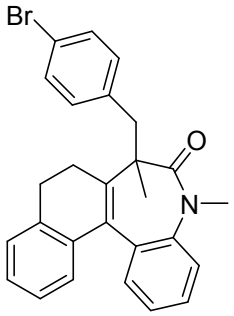


7-(4-chlorobenzyl)-5,7-Dimethyl-5,7,8,9-tetrahydro-6*H*-benzo[*b*]naphtho[1,2-*d*]azepin-6-one (3bb)

pale green solid, 66 mg, 80% yield; m. p. 209 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.43 (d, *J* =

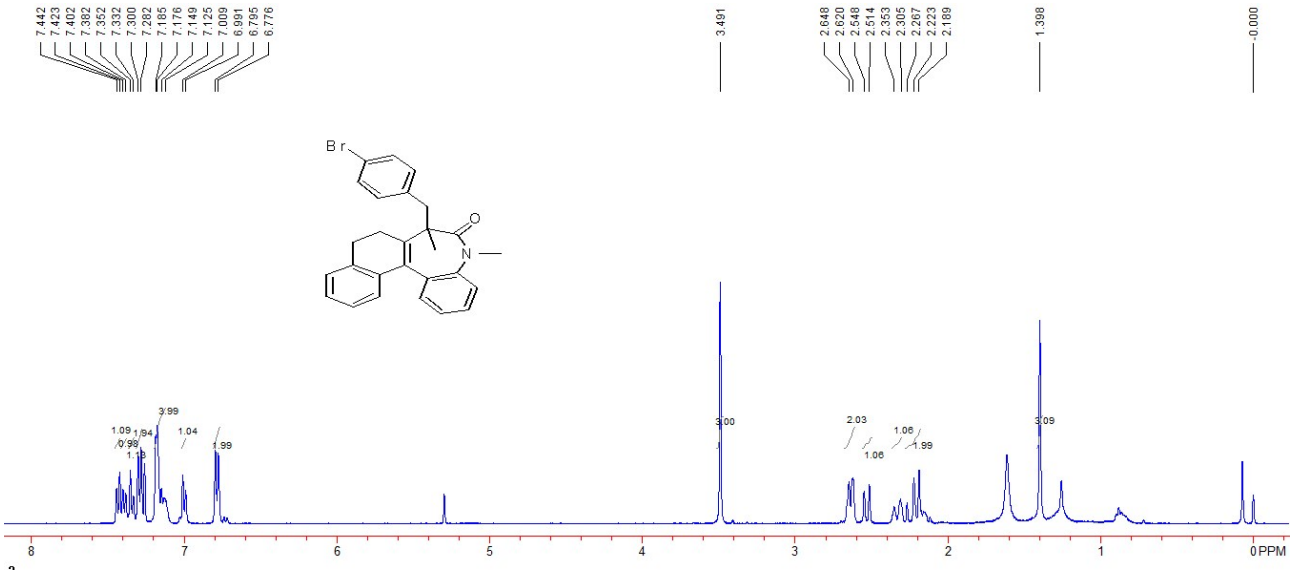
8.0 Hz, 1H), 7.39 (d, *J* = 7.6 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.19-7.13 (m, 6H), 7.00 (d, *J* = 7.6 Hz, 1H), 6.84 (d, *J* = 8.0 Hz, 2H), 3.49 (s, 3H), 2.66-2.62 (m, 2H), 2.55 (d, *J* = 13.6 Hz, 1H), 2.35-2.31 (m, 1H), 2.24-2.16 (m, 2H), 1.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 173.4, 142.6, 142.2, 136.7, 136.6, 136.4, 132.9, 132.6, 132.2, 131.2, 130.1, 128.5, 128.0, 127.1, 127.0, 126.8, 126.1, 124.0, 121.6, 51.7, 38.2, 36.8, 28.4, 26.2, 22.6; IR (CH_2Cl_2): ν 2958, 2922, 1644, 1596, 1579, 1492, 1445, 1350, 1299, 1254, 1241, 1090, 1050, 874, 820, 762, 723, 703, 675, 668 cm^{-1}; HRMS (ESI) Calcd. For $C_{27}H_{25}ClNO$ $(M+H)^+$ requires: 414.1619, Found: 414.1615.

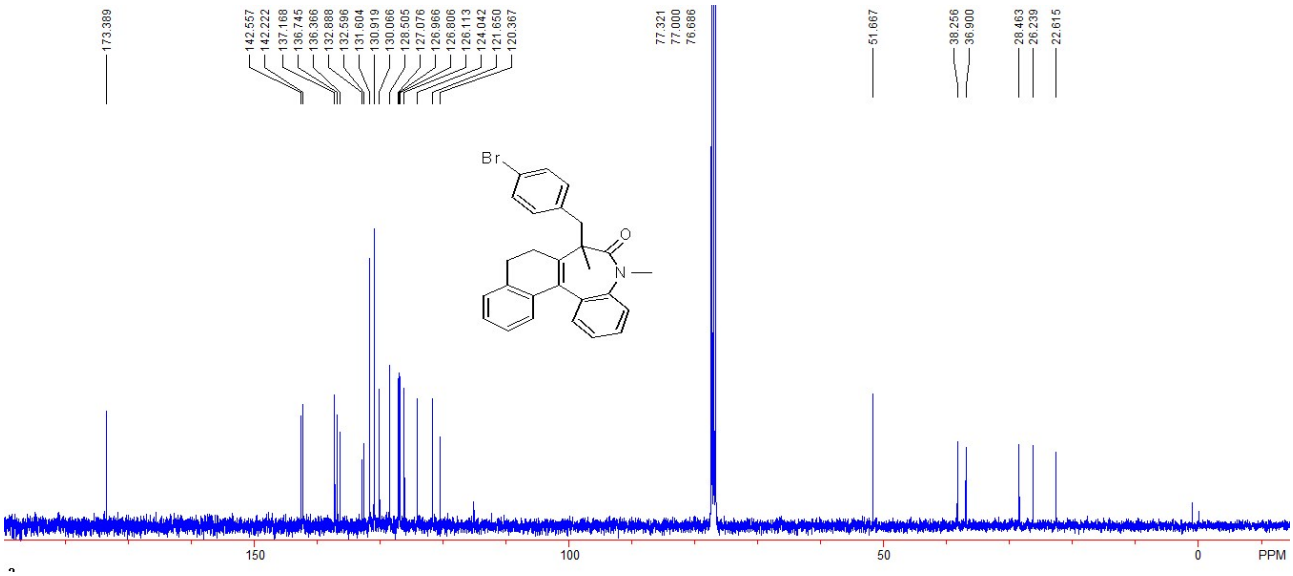


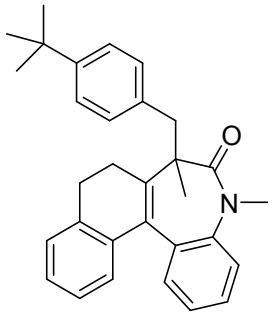


7-(4-bromobenzyl)-5,7-Dimethyl-5,7,8,9-tetrahydro-6*H*-benzo[*b*]naphtho[1,2-*d*]azepin-6-one (3bc)

pale green solid, 69 mg, 75% yield; m. p. 190 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.43 (d, *J* = 7.6 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.29 (d, *J* = 7.2 Hz, 2H), 7.19-7.13 (m, 4H), 7.00 (d, *J* = 7.2 Hz, 1H), 6.79 (d, *J* = 7.6 Hz, 2H), 3.49 (s, 3H), 2.65-2.62 (m, 2H), 2.53 (d, *J* = 13.6 Hz, 1H), 2.35-2.27 (m, 1H), 2.22-2.19 (m, 2H), 1.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 173.4, 142.6, 142.2, 137.2, 136.7, 136.4, 132.9, 132.6, 131.6, 130.9, 130.1, 128.5, 127.1, 127.0, 126.8, 126.1, 124.0, 121.7, 120.4, 51.7, 38.3, 36.9, 28.5, 26.2, 22.6; IR (CH_2Cl_2): ν 2957, 2924, 1647, 1622, 1596, 1584, 1488, 1444, 1380, 1361, 1265, 1221, 1071, 1049, 1011, 825, 808, 765, 747, 736, 729, 669 cm^{-1}; HRMS (ESI) Calcd. For $C_{27}H_{25}BrNO$ $(M+H)^+$ requires: 458.1114, Found: 458.1111.

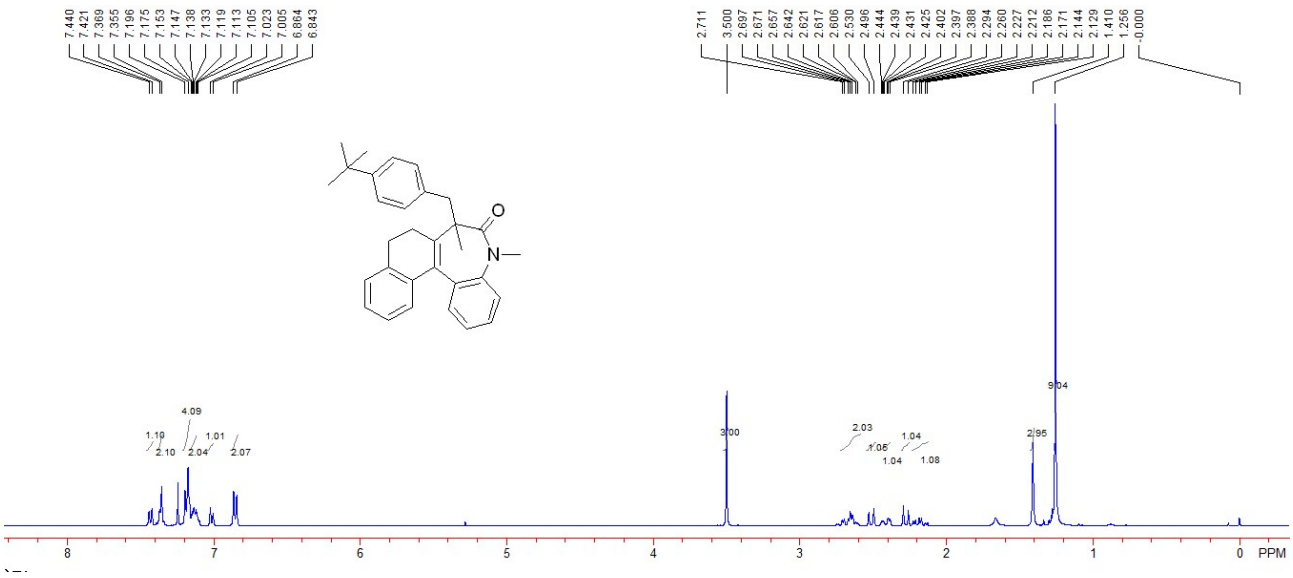


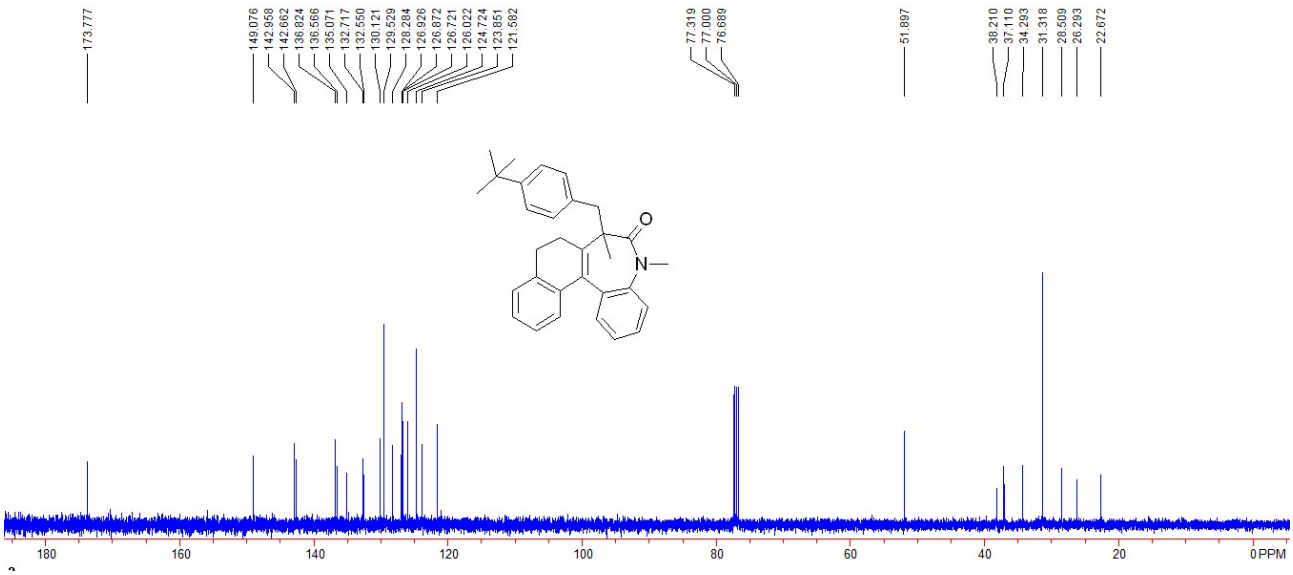


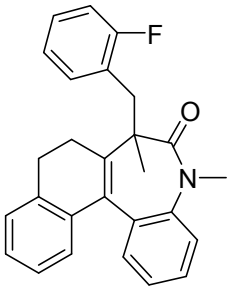


7-(4-(tert-butyl)benzyl)-5,7-Dimethyl-5,7,8,9-tetrahydro-6*H*-benzo[*b*]naphtho[1,2-*d*]azepin-6-one (3bd)

pale green solid, 83 mg, 95% yield; m. p. 187 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.43 (d, *J* = 7.6 Hz, 1H), 7.37-7.36 (m, 2H), 7.20-7.15 (m, 4H), 7.15-7.11 (m, 2H), 7.01 (d, *J* = 7.2 Hz, 1H), 6.85 (d, *J* = 8.4 Hz, 2H), 3.50 (s, 3H), 2.71-2.61 (m, 2H), 2.51 (d, *J* = 13.6 Hz, 1H), 2.44-2.39 (m, 1H), 2.28 (d, *J* = 13.6 Hz, 1H), 2.18 (td, J_1 = 6.0 Hz, J_2 = 16.4 Hz, 1H), 1.41 (s, 3H), 1.26 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 173.8, 149.1, 143.0, 142.7, 136.8, 136.6, 135.1, 132.7, 132.6, 130.1, 129.5, 128.3, 126.93, 126.87, 126.7, 126.0, 124.7, 123.9, 121.6, 51.9, 38.2, 37.1, 34.3, 31.3, 28.5, 26.3, 22.7; IR (CH_2Cl_2): ν 2959, 2921, 1647, 1597, 1495, 1445, 1350, 1253, 839, 812, 766, 749, 728, 669 cm^{-1}; HRMS (ESI) Calcd. For $C_{31}H_{34}NO$ $(M+H)^+$ requires: 436.2635, Found: 436.2629.



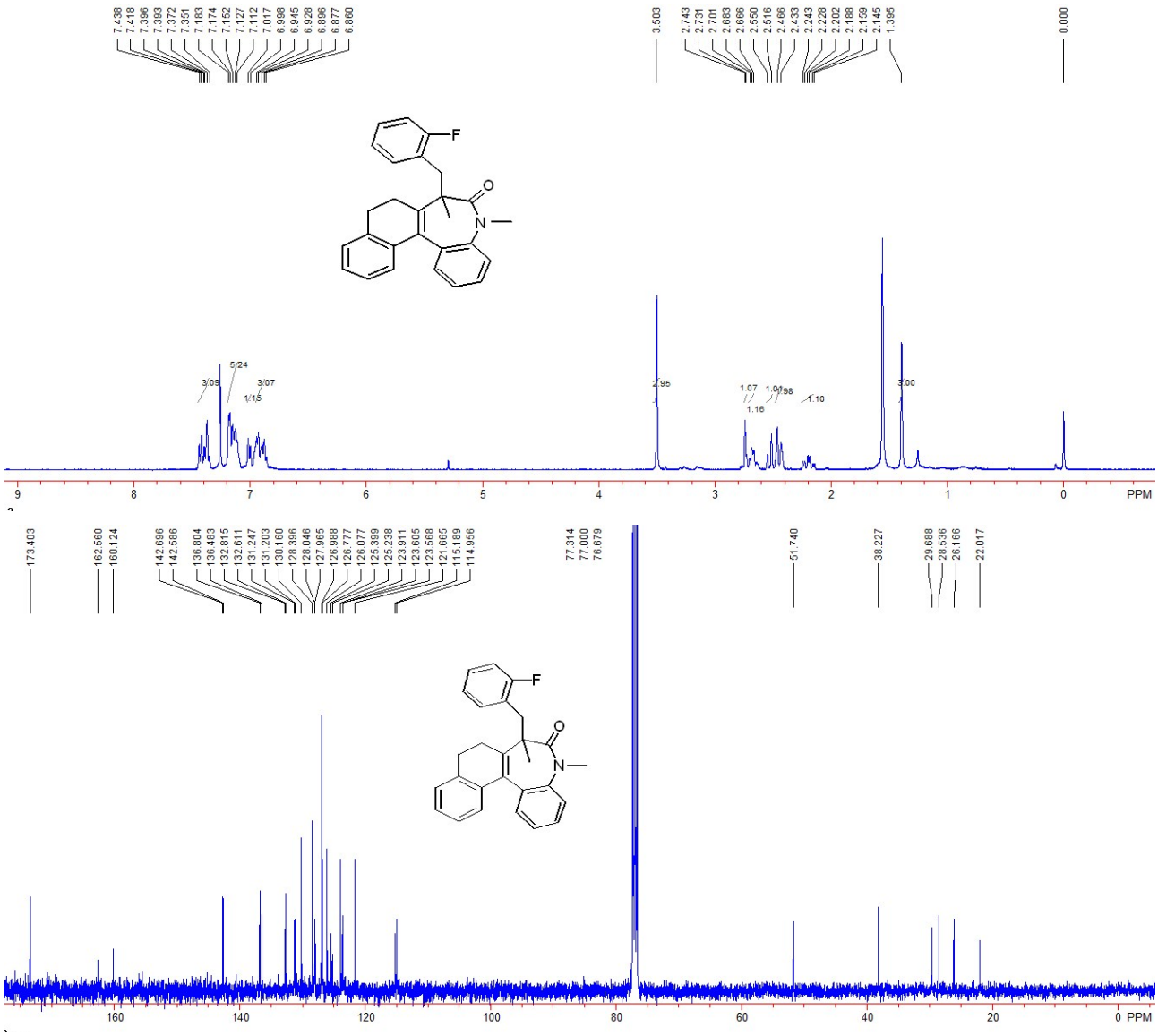


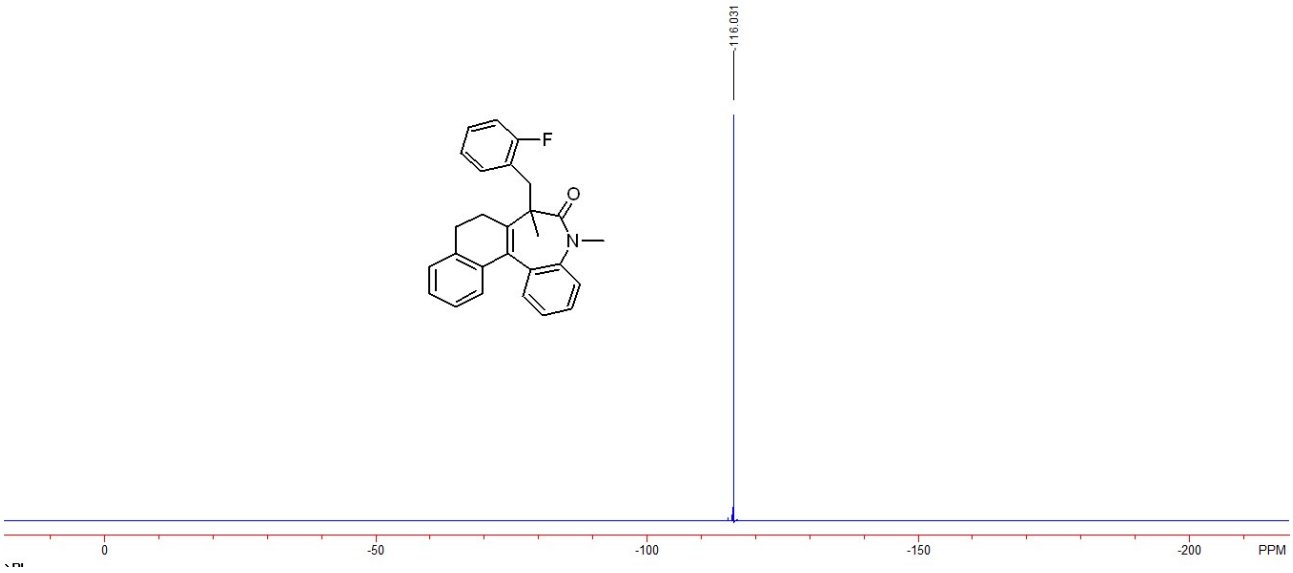


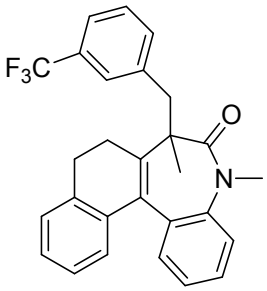
7-(2-fluorobenzyl)-5,7-Dimethyl-5,7,8,9-tetrahydro-6*H*-benzo[*b*]naphtho[1,2-*d*]azepin-6-one (3bf)

pale green solid, 54 mg, 68% yield; m. p. 210 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.44-7.35 (m, 3H), 7.18-7.11 (m, 5H), 7.01 (d, J = 7.6 Hz, 1H), 6.95-6.86 (m, 3H), 3.50 (s, 3H), 2.74-2.73 (m, 1H), 2.68 (t, J = 7.2 Hz, 1H), 2.53 (d, J = 13.6 Hz, 1H), 2.45 (d, J = 13.2 Hz, 2H), 2.19 (td, J_1 = 5.6

Hz, J_2 = 16.4 Hz, 1H), 1.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 173.4, 161.3 (d, J = 243.6 Hz), 142.7, 142.6, 136.8, 136.5, 132.7 (d, J = 20.4 Hz), 131.2, 131.2, 130.2, 128.4, 128.0 (d, J = 8.1 Hz), 127.0, 126.8, 126.1, 125.4, 125.2, 123.9, 123.6 (d, J = 3.7 Hz), 121.7, 115.1 (d, J = 23.3 Hz), 51.7, 38.2, 29.7, 28.5, 26.2, 22.0; ^{19}F NMR (376 MHz, $CDCl_3$): δ -116.0; IR (CH_2Cl_2): ν 2972, 2925, 1650, 1492, 1452, 1381, 1354, 1257, 1085, 1046, 879, 762, 668, 653 cm^{-1}; HRMS (ESI) Calcd. For $C_{27}H_{25}FNO$ $(M+H)^+$ requires: 398.1915, Found: 398.1914.

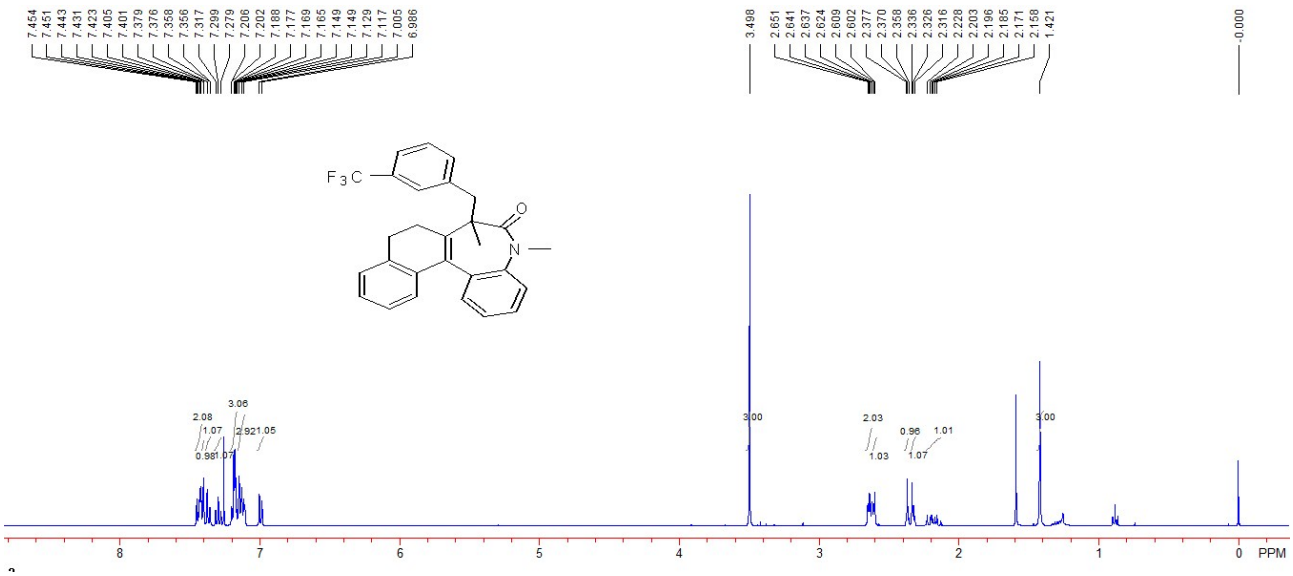






5,7-Dimethyl-7-(3-(trifluoromethyl)benzyl)-5,7,8,9-tetrahydro-6*H*-benzo[*b*]naphtho[1,2-*d*]azepin-6-one (3bh)

pale green solid, 59 mg, 66% yield; m. p. 229 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.45-7.42 (m, 2H), 7.40 (d, J = 1.6 Hz, 1H), 7.37 (dd, J_1 = 1.2 Hz, J_2 = 8.0 Hz, 1H), 7.30 (t, J = 7.6 Hz, 1H), 7.21-7.17 (m, 3H), 7.15-7.12 (m, 3H), 6.99 (d, J = 7.6 Hz, 1H), 3.50 (s, 3H), 2.65-2.62 (m, 2H), 2.62-2.60 (m, 1H), 2.38-2.36 (m, 1H), 2.34-2.32 (m, 1H), 2.23-2.16 (m, 1H), 1.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 173.1, 142.5, 142.0, 139.1, 136.7, 136.3, 133.3, 133.1, 132.6, 130.2 (q, J = 32.0 Hz), 130.1, 128.6, 128.2, 124.1 (q, J = 270.6 Hz), 127.1, 127.0, 126.8, 126.5 (q, J = 3.7 Hz), 126.1, 124.1, 123.2 (q, J = 3.6 Hz), 121.6, 51.7, 38.2, 37.5, 28.3, 26.3, 22.7; ^{19}F NMR (376 MHz, $CDCl_3$): δ -62.6; IR (CH_2Cl_2): ν 2918, 2902, 1648, 1595, 1493, 1446, 1351, 1329, 1162, 1120, 1096, 1074, 898, 805, 764, 749, 729, 703, 670, 658 cm^{-1}; HRMS (ESI) Calcd. For $C_{28}H_{25}F_3NO$ $(M+H)^+$ requires: 448.1883, Found: 448.1878.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7.129
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2.651
2.641
2.637
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2.203
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2.185
2.171
2.158
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0.98
1.07
3.06
2.92
1.05
3.00
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3.00
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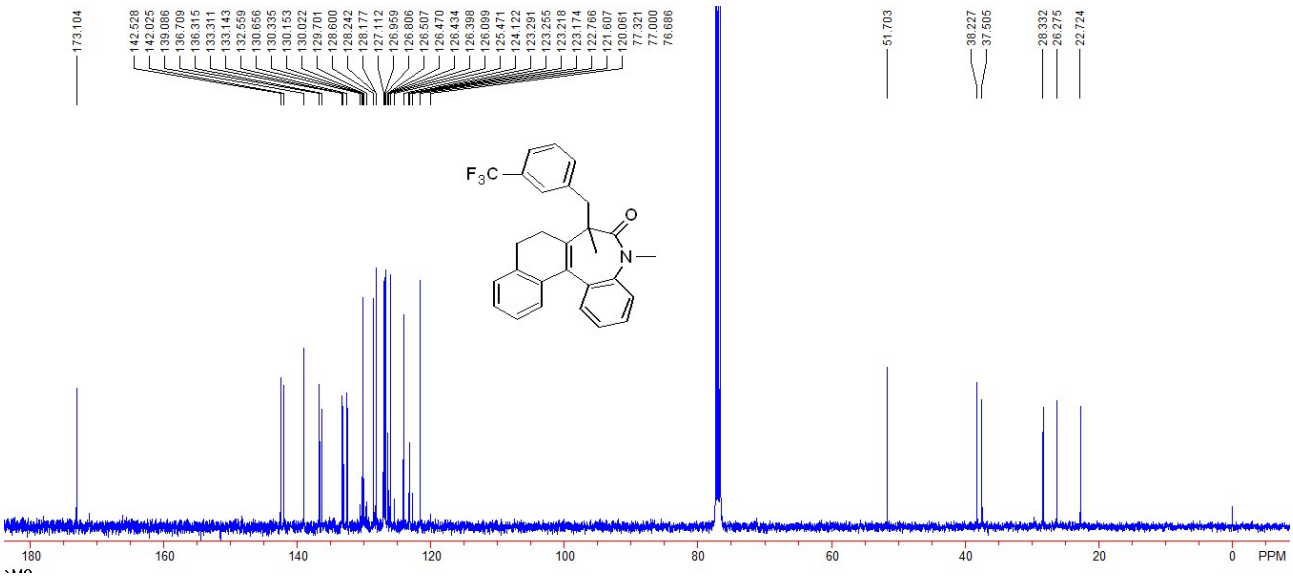
PPM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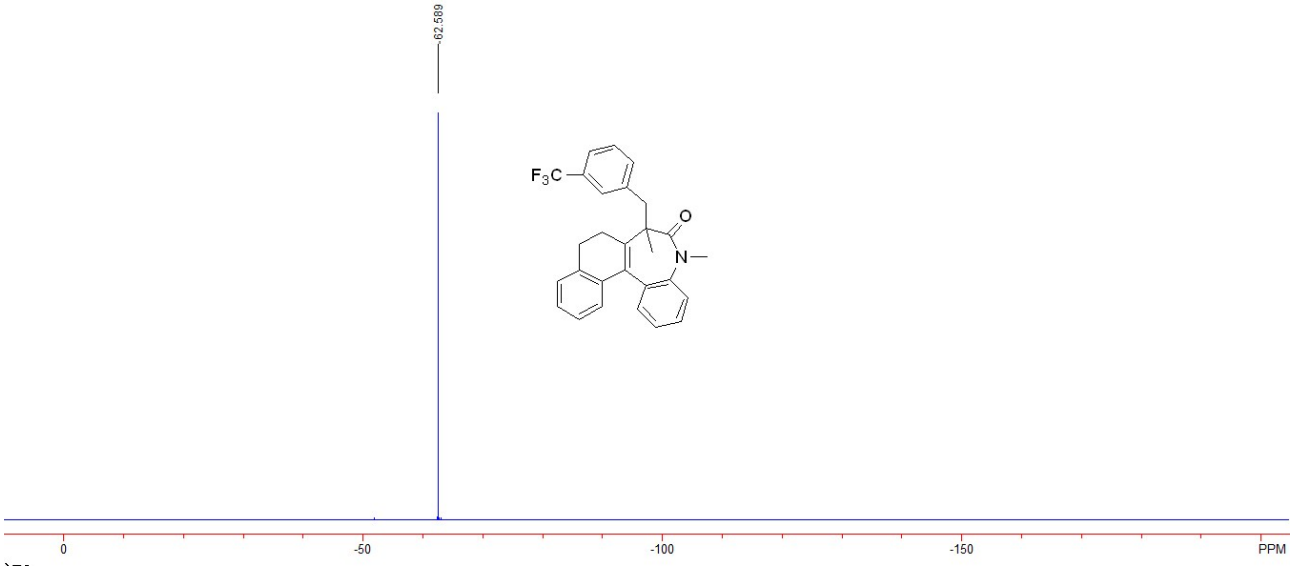
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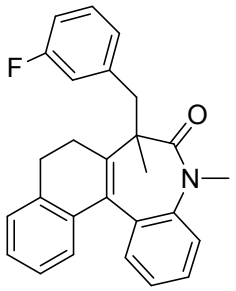
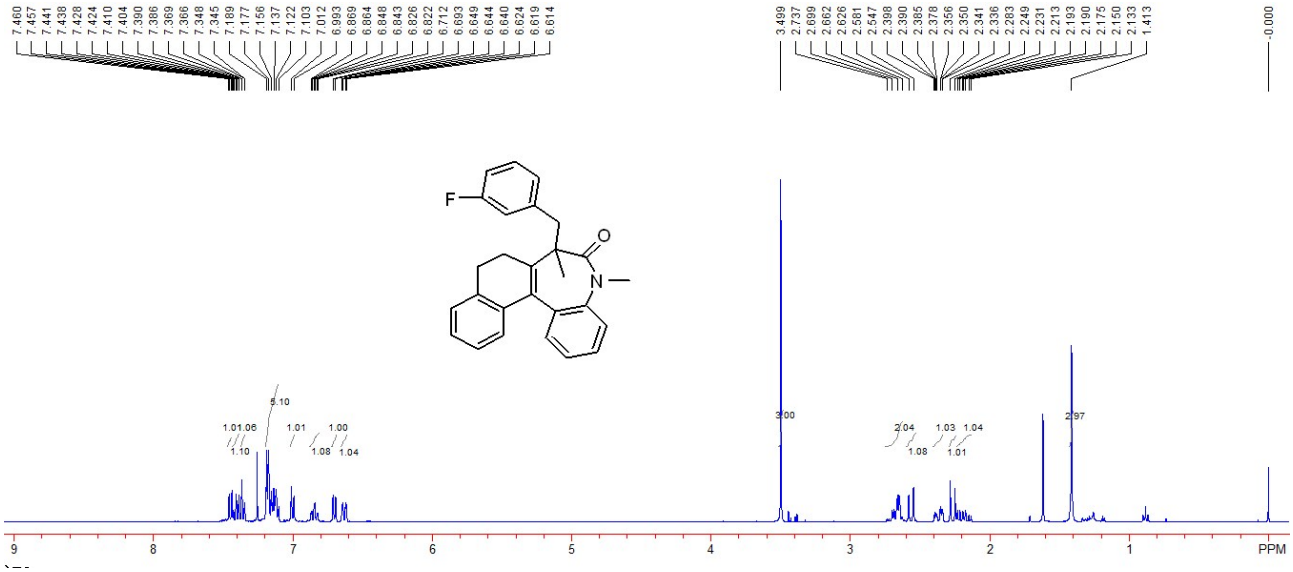
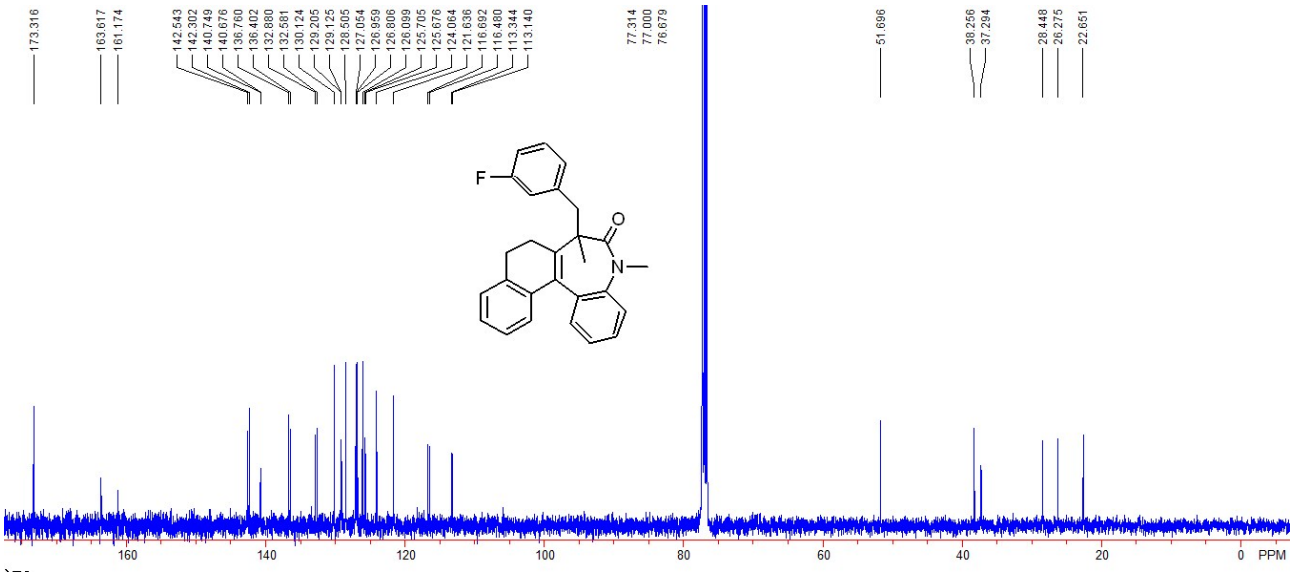
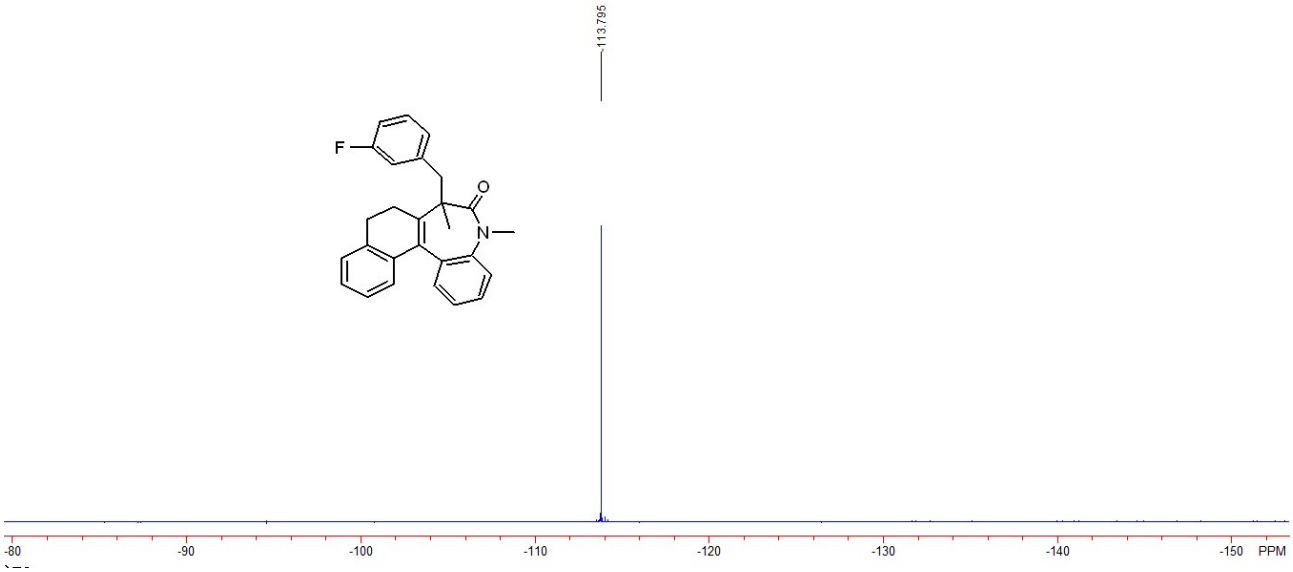


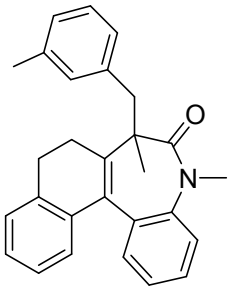
7-(3-fluorobenzyl)-5,7-Dimethyl-5,7,8,9-tetrahydro-6*H*-benzo[*b*]naphtho[1,2-*d*]azepin-6-one (3bi)

pale green solid, 61 mg, 76% yield; m. p. 219 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.45 (dd, J_1 = 1.2 Hz, J_2 = 7.6 Hz, 1H), 7.43-7.39 (m, 1H), 7.36 (dd, J_1 = 1.2 Hz, J_2 = 8.4 Hz, 1H), 7.19-7.10 (m, 5H), 7.00 (d, J = 7.6 Hz, 1H), 6.84 (td, J_1 = 2,0 Hz, J_2 = 8.4 Hz, 1H), 6.70 (d, J = 7.6 Hz, 1H), 6.63 (dt, J_1 = 3.6 Hz, J_2 = 10.0 Hz, 1H), 3.50 (s, 3H), 2.74-2.63 (m, 2H), 2.56 (d, J = 13.6 Hz, 1H), 2.40-2.34 (m, 1H), 2.27 (d, J = 13.6 Hz, 1H), 2.18 (td, J_1 = 7.6 Hz, J_2 = 15.2 Hz, 1H), 1.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 173.3, 162.4 (d, J = 244.3 Hz), 142.5, 142.3, 140.7 (d, J = 7.4 Hz), 136.7, 136.4, 132.9, 132.6, 130.1, 129.2 (d, J = 8.0 Hz), 128.5, 127.1, 127.0, 126.8, 126.1, 125.7 (d, J = 2.9 Hz), 124.1, 121.6, 116.6 (d, J = 21.2 Hz), 113.2 (d, J = 20.4 Hz), 51.7, 38.3, 37.3, 28.4, 26.3, 22.7; ^{19}F NMR (376 MHz, $CDCl_3$): δ -113.8; IR (CH_2Cl_2): ν 2958, 2921, 1643, 1594, 1492, 1466, 1350, 1255, 1242, 1091, 1076, 1050, 876, 820, 772, 752, 724, 705, 668 cm^{-1}; HRMS (ESI) Calcd. For $C_{27}H_{25}FNO$ $(M+H)^+$ requires: 398.1915, Found: 398.1912.





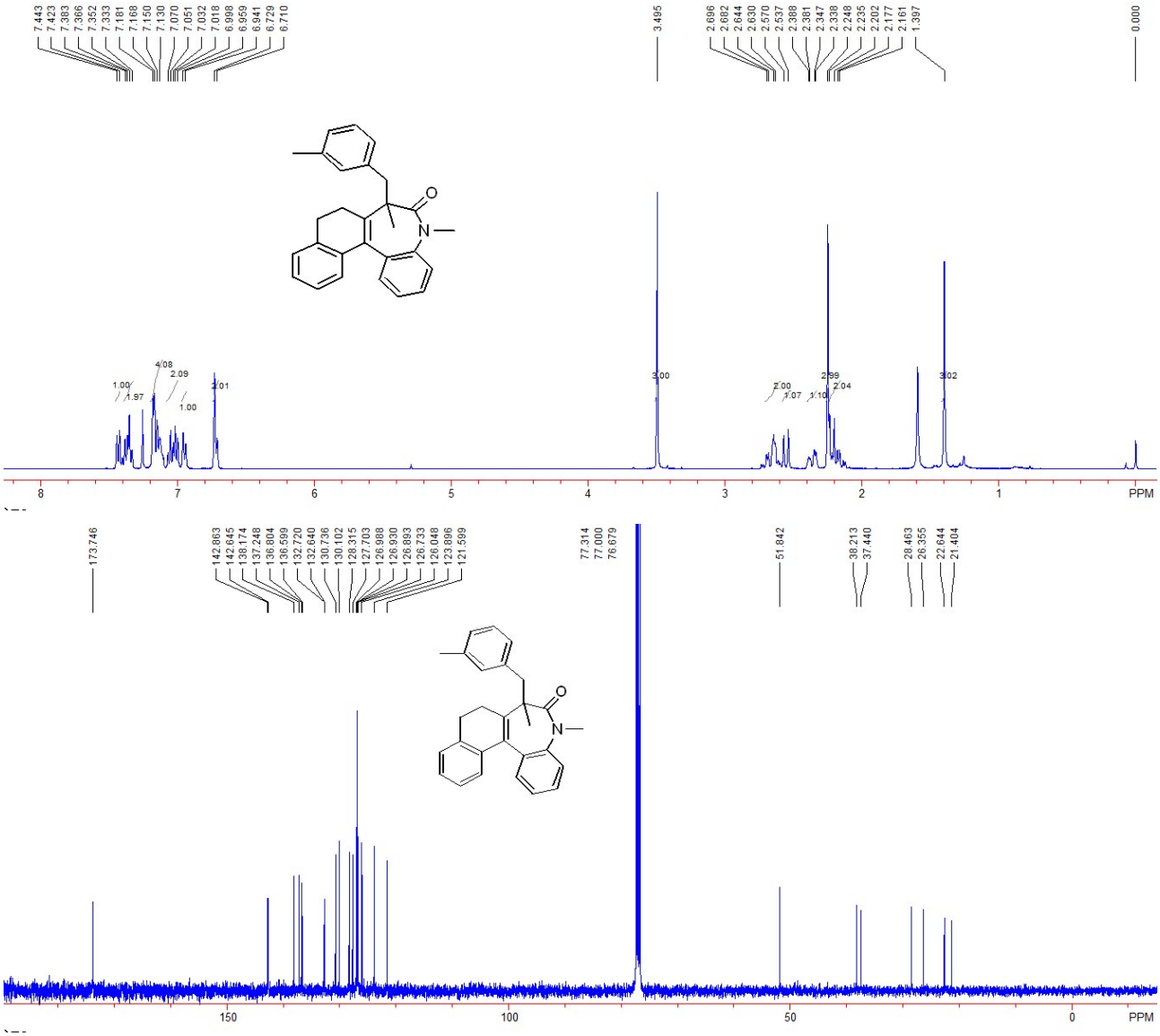




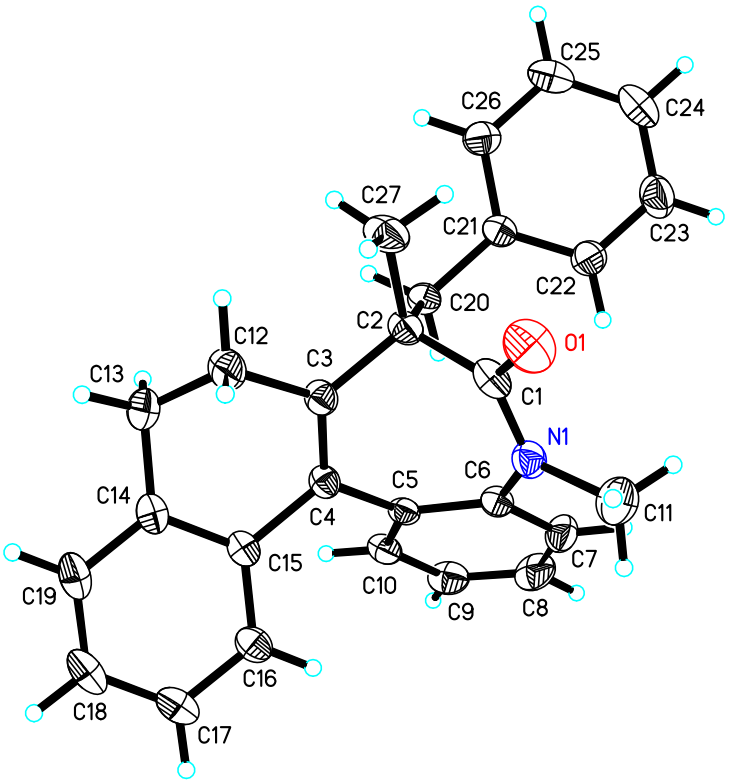
5,7-Dimethyl-7-(3-methylbenzyl)-5,7,8,9-tetrahydro-6*H*-benzo[*b*]naphtho[1,2-*d*]azepin-6-one (3bj)

green solid, 59 mg, 73% yield; m. p. 222 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.43 (d, *J* = 8.0 Hz, 1H), 7.38-7.33 (m, 2H), 7.18-7.11 (m, 4H), 7.05 (t, *J* = 7.6 Hz, 1H), 7.00 (d, *J* = 8.0 Hz, 1H), 6.95 (d, *J* = 7.2 Hz, 1H), 6.72 (d, *J* = 7.6 Hz, 2H), 3.50 (s, 3H), 2.70-2.60 (m, 2H), 2.55 (d, *J* = 13.2

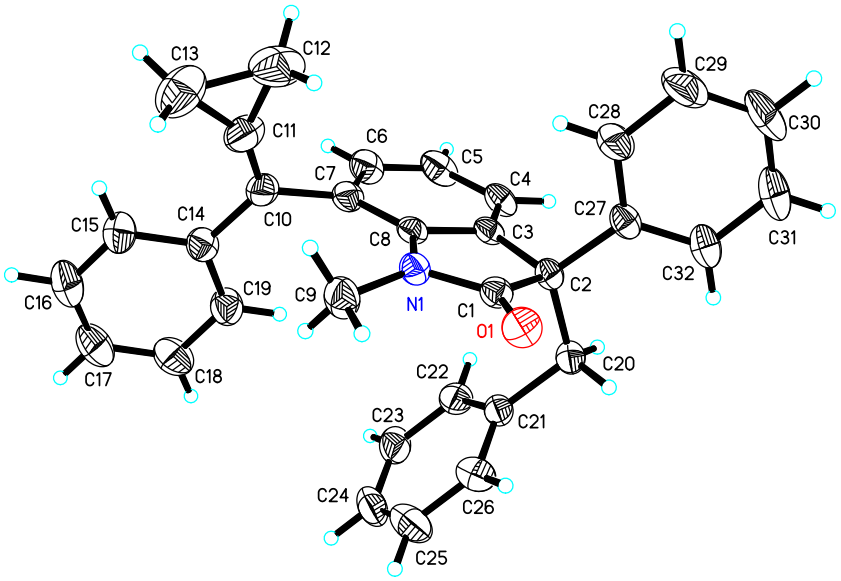
Hz, 1H), 2.39-2.34 (m, 1H), 2.25 (s, 3H), 2.24-2.16 (m, 2H), 1.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 173.7, 142.9, 142.6, 138.2, 137.2, 136.8, 136.6, 132.7, 132.6, 130.7, 130.1, 128.3, 127.7, 127.0, 126.93, 126.89, 126.7, 126.0, 123.9, 121.6, 51.8, 38.2, 37.4, 28.5, 26.4, 22.6, 21.4; IR (CH_2Cl_2): ν 2917, 2850, 1648, 1595, 1494, 1485, 1447, 1418, 1379, 1350, 1299, 1253, 1232, 1081, 1049, 800, 774, 763, 750, 727, 699, 669, 654 cm^{-1}; HRMS (ESI) Calcd. For $C_{28}H_{28}NO$ $(M+H)^+$ requires: 394.2165, Found: 394.2161.



4. X-ray data



The crystal data of **3aa** have been deposited in CCDC with number 1545252. Empirical Formula: $C_{27}H_{25}NO$; Formula Weight: 379.48; Crystal Color, Habit: colorless; Crystal Dimensions: 0.200 x 0.170 x 0.140 mm^3; Crystal System: Monoclinic; Lattice Parameters: a = 13.379(5) Å, alpha = 90 deg. b = 9.939(3) Å, beta = 91.100(8) deg. c = 15.142(5) Å, gamma = 90 deg; V = 2013.1(12) $Å^3$; Space group: P 21/n; Z = 4; D_{calc} = 1.252 g/cm^3; F_{000} = 808; Diffractometer: Rigaku AFC7R; Residuals: R; R_w: 0.0530, 0.1220.



The crystal data of **3as'** have been deposited in CCDC with number 1552527. Empirical Formula: $C_{32}H_{27}NO$; Formula Weight: 441.54; Crystal Color, Habit: colorless; Crystal Dimensions: 0.220 x 0.170 x 0.140 mm^3; Crystal System: Triclinic; Lattice Parameters: a = 9.1032(15) Å, alpha = 94.100(4) deg. b = 14.843(2) Å, beta = 101.550(4) deg. c = 19.069(3) Å, gamma = 104.178(3) deg; V = 2427.7(7) $Å^3$; Space group: P -1; Z = 4; D_{calc} = 1.208 g/cm^3; F_{000} = 936; Diffractometer: Rigaku AFC7R; Residuals: R; R_w: 0.0641, 0.1494.

5. References.

1) L.-Z. Yu, Q. Xu, X.-Y. Tang and M. Shi. *ACS Catalysis*. 2016, 6, 526.

2) For recent reviews on diaryliodonium salts, see: (a) Deprez, N. R.; Sanford, M. S. *Inorg. Chem.* 2007, 46, 1924. (b) Bielawski, M.; Zhu, M.; Olofsson, B. *Adv. Synth. Catal.* 2007, 349, 2610. (c) Merritt, E. A.; Olofsson, B. *Angew. Chem., Int. Ed.* 2009, 48, 9052. (d) Hickman, A. J.; Sanford, M. S. *Nature.* 2012, 484, 177.