Supporting Information for

Novel and Facile Synthesis of 1-Benzazepines via Copper-Catalyzed Oxidative C(sp^3)-H/C(sp^2)-H Cross-Coupling

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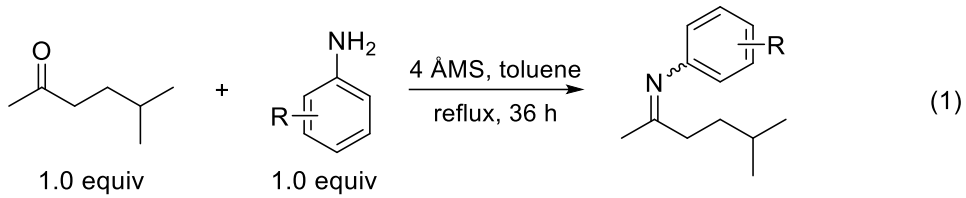
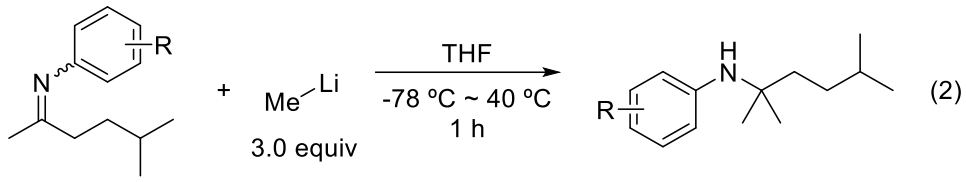
I. General Information: Instrumentation, Materials.

Instrumentation. ^{1}H NMR spectra were recorded at ambient temperature on Bruker-400 (400 MHz) spectrometers and are referenced relative to the residual protons in $CDCl_3$ at δ 7.26 ppm or $(CD_3)_2SO$-d_6 at δ 2.50 ppm. Data for ^{1}H NMR are reported as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, ap = apparent), integration, and coupling constant (Hz). ^{13}C NMR spectra were recorded at ambient temperature on Bruker-400 (100 MHz) spectrometers and are referenced relative to $CDCl_3$ at δ 77.16 ppm or $(CD_3)_2SO$-d_6 at δ 39.52 ppm. The ^{13}C NMR spectra were obtained with 1H decoupling. Data for ^{13}C NMR are reported in terms of chemical shift and multiplicity where appropriate. High resolution mass spectra were recorded on P-SIMS-Gly of BrukerDaltonics Inc. using ESI-TOF (electrospray ionization-time of flight). Infrared spectra were recorded on a Thermo Scientific Nicolet iS10 as either neat films or solids. Melting points were determined on a melting point apparatus and are uncorrected.

Materials. Cupric oxide was purchased from Energy Chemical and used as received. Silver acetate was purchased from Beijing HWRK Chem Co., LTD and used as recieved. Sodium bicarbonate, sodium sulfate and 1,2-dichloroethane were purchased from Sinopharm Chemical Reagent Co., Ltd and used as received. Other commercial reagents were purchased from commercial suppliers and used without further purification.

II. Preparation of Substrates.



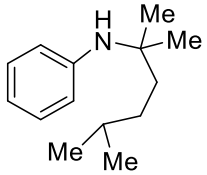


Genaral procedure (A) for the synthesis of substrates.

Step 1: Preparation of imines. To an oven-dried round-bottom bottle equipped with a magnetic stir bar was added ketone (1.0 equiv), aniline (1.0 equiv), 4 ÅMS (0.2 g/mmol) and toluene (2.0 M). The mixture was then reflux for 36 h. After completion, it was allowed to cool to room temperature, and was directly filtered through a short pad of Celite®, washed with EtOAc. The filtrate was concentrated under vacuum and was used directly.

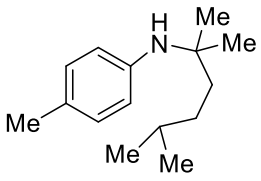
Step 2: Preparation of the substates. Methyllithium (1.6 M in diethyl ether, 3.0 equiv) was added dropwise to a vigorously stirred solution of imine in THF (0.1 M) at -78 °C under N_2 atmosphere and then stirred at 40°C for 1 h (but with **1f** and **1k**, the stirring temperature was 0°C). After completion, the reaction was quenched with water. The resulting aqueous layer was extracted with EtOAc for 3 times and the combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated under vacuum. The crude material was purified by column chromatography on silica gel to give the substrate **1**.

***N*-(2,5-dimethylhexan-2-yl)aniline (1a)**



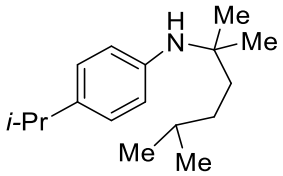
Prepared according to general procedure (A) from aniline to provide the title compound **1a** as a colorless oil (1.11 g, 5.5 mmol, 55% total yield). IR (neat, cm^{-1}) 3412, 2954, 2929, 2868, 1599, 1496, 1467, 1427, 1383, 1365, 1320, 1258, 1237, 1215, 1179, 1115, 1082, 1031, 995, 867, 743, 691. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (ddd, *J* = 8.1, 6.2, 2.8 Hz, 2H), 6.76 – 6.67 (m, 3H), 3.45 (s, 1H), 1.66 – 1.57 (m, 2H), 1.47 (dq, *J* = 13.1, 6.6 Hz, 1H), 1.28 (s, 6H), 1.26 – 1.18 (m, 2H), 0.86 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.1, 129.0, 118.0, 117.0, 53.9, 39.7, 33.2, 28.6, 28.5, 22.8. HRMS (ESI) calcd. for $C_{14}H_{24}N$ $[M+H]^+$ *m/z* 206.1909, found 206.1908.

***N*-(2,5-dimethylhexan-2-yl)-4-methylaniline (1b)**



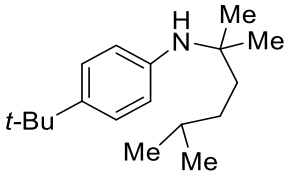
Prepared according to general procedure (A) from *p*-toluidine to provide the title compound **1b** as a colorless oil (1.38 g, 6.3 mmol, 63% total yield). IR (neat, cm^{-1}) 2954, 2926, 2867, 1617, 1513, 1467, 1383, 1365, 1304, 1254, 1237, 1182, 1114, 1081, 806. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96 (d, *J* = 8.1 Hz, 2H), 6.67 (d, *J* = 8.3 Hz, 2H), 2.58 (s, 1H), 2.24 (s, 3H), 1.64 – 1.52 (m, 2H), 1.48 (dt, *J* = 13.2, 6.6 Hz, 1H), 1.27 – 1.19 (m, 8H), 0.87 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.4, 129.5, 128.0, 118.5, 54.1, 39.9, 33.3, 28.7, 28.4, 22.9, 20.6. HRMS (ESI) calcd. for $C_{15}H_{26}N$ $[M+H]^+$ *m/z* 220.2065, found 220.2069.

_N_-(2,5-dimethylhexan-2-yl)-4-isopropylaniline (1c)



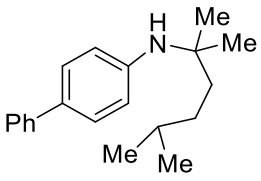
Prepared according to general procedure (A) from 4-isopropylaniline to provide the title compound **1c** as a yellow oil (0.96 g, 3.9 mmol, 39% total yield). IR (neat, cm^{-1}) 2955, 2929, 2868, 1614, 1514, 1466, 1382, 1364, 1318, 1290, 1255, 1238, 1214, 1185, 1115, 1081, 1055, 818, 727. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01 (d, *J* = 8.4 Hz, 2H), 6.68 (d, *J* = 8.4 Hz, 2H), 2.80 (dt, *J* = 13.8, 6.9 Hz, 1H), 2.71 (s, 1H), 1.62 – 1.54 (m, 2H), 1.47 (dq, *J* = 13.6, 6.8 Hz, 1H), 1.28 – 1.23 (m, 8H), 1.21 (d, *J* = 6.9 Hz, 6H), 0.87 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.7, 138.9, 126.8, 117.9, 54.0, 40.0, 33.3, 33.2, 28.6, 28.4, 24.3, 22.8. HRMS (ESI) calcd. for $C_{17}H_{30}N$ $[M+H]^+$ *m/z* 248.2378, found 248.2378.

4-(*tert*-butyl)-*N*-(2,5-dimethylhexan-2-yl)aniline (1d)



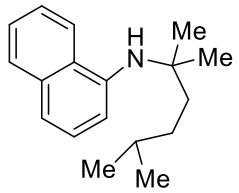
Prepared according to general procedure (A) from 4-(tert-butyl)aniline to provide the title compound **1d** as a yellow oil (1.02 g, 3.9 mmol, 39% total yield). IR (neat, cm^{-1}) 2954, 2927, 2867, 1614, 1515, 1466, 1383, 1363, 1321, 1305, 1257, 1194, 1113, 1081, 818, 730. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (d, *J* = 8.6 Hz, 2H), 6.69 (d, *J* = 8.6 Hz, 2H), 3.36 (s, 1H), 1.63 – 1.56 (m, 2H), 1.49 (dt, *J* = 13.1, 6.6 Hz, 1H), 1.29 (s, 9H), 1.27 – 1.20 (m, 8H), 0.88 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.1, 141.0, 125.6, 117.3, 53.9, 39.8, 33.9, 33.1, 31.6, 28.5, 28.2, 22.7. HRMS (ESI) calcd. for $C_{18}H_{32}N$ $[M+H]^+$ *m/z* 262.2535, found 262.2537.

_N_-(2,5-dimethylhexan-2-yl)-[1,1'-biphenyl]-4-amine (1e)



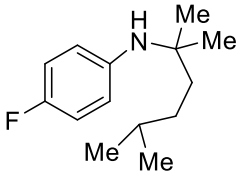
Prepared according to general procedure (A) from [1,1'-biphenyl]-4-amine to provide the title compound **1e** as a colorless oil (1.35 g, 4.8 mmol, 48% total yield). IR (neat, cm^{-1}) 3413, 2953, 2927, 2867, 1610, 1521, 1486, 1467, 1442, 1383, 1365, 1320, 1299, 1273, 1254, 1237, 1177, 1113, 1076, 822, 759, 695. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.4 Hz, 2H), 7.44 – 7.33 (m, 4H), 7.24 (t, *J* = 7.3 Hz, 1H), 6.77 (d, *J* = 8.5 Hz, 2H), 3.08 (s, 1H), 1.73 – 1.60 (m, 2H), 1.48 (dq, *J* = 12.8, 6.5 Hz, 1H), 1.32 (s, 6H), 1.28 – 1.18 (m, 2H), 0.88 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.5, 141.3, 130.4, 128.7, 127.7, 126.4, 126.1, 116.7, 53.9, 39.6, 33.2, 28.6, 28.4, 22.8. HRMS (ESI) calcd. for $C_{20}H_{28}N$ $[M+H]^+$ *m/z* 282.2222, found 282.2222.

_N_-(2,5-dimethylhexan-2-yl)naphthalen-1-amine (1f)



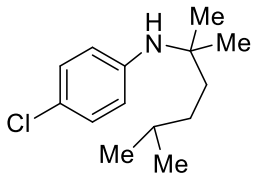
Prepared according to general procedure (A) from naphthalen-1-amine to provide the title compound **1f** as a yellow oil (1.25 g, 4.9 mmol, 49% total yield). IR (neat, cm^{-1}) 3451, 3057, 2953, 2927, 2867, 1578, 1526, 1486, 1463, 1408, 1384, 1365, 1343, 1281, 1225, 1170, 1115, 1099, 1026, 781, 766. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.76 (m, 2H), 7.48 – 7.40 (m, 2H), 7.34 (t, J = 7.9 Hz, 1H), 7.25 (d, J = 8.3 Hz, 1H), 6.92 (d, J = 7.6 Hz, 1H), 4.23 (s, 1H), 1.86 – 1.77 (m, 2H), 1.54 (dt, J = 13.2, 6.6 Hz, 1H), 1.45 (s, 6H), 1.35 – 1.25 (m, 2H), 0.92 (s, 3H), 0.90 (s, 3H).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.8, 134.8, 129.0, 126.4, 125.5, 125.0, 124.7, 120.3, 117.4, 108.7, 54.0, 39.5, 33.2, 28.6, 28.2, 22.8. HRMS (ESI) calcd. for $C_{18}H_{26}N$ $[M+H]^+$ m/z 256.2065, found 256.2057.

_N_-(2,5-dimethylhexan-2-yl)-4-fluoroaniline (1g)



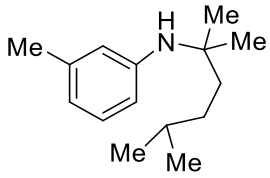
Prepared according to general procedure (A) from 4-fluoroaniline to provide the title compound **1g** as a yellow oil (1.12 g, 5.0 mmol, 50% total yield). IR (neat, cm^{-1}) 2955, 2930, 2869, 1613, 1505, 1468, 1384, 1366, 1320, 1212, 1183, 1115, 1101, 818, 786. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.91 – 6.81 (m, 2H), 6.70 (ddd, *J* = 6.8, 5.3, 3.0 Hz, 2H), 2.75 (s, 1H), 1.58 – 1.51 (m, 2H), 1.47 (dt, *J* = 13.2, 6.7 Hz, 1H), 1.27 – 1.18 (m, 8H), 0.87 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.1 (d, *J* = 236.9 Hz), 142.9, 120.0 (d, *J* = 7.5 Hz), 115.4 (d, *J* = 22.0 Hz), 54.3, 39.7, 33.2, 28.6, 28.4, 22.8. HRMS (ESI) calcd. for $C_{14}H_{23}NF$ $[M+H]^+$ *m/z* 224.1815, found 224.1814.

4-chloro-*N*-(2,5-dimethylhexan-2-yl)aniline (1h)



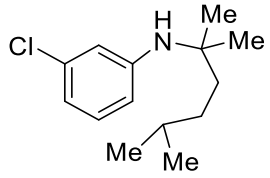
Prepared according to general procedure (A) from 4-chloroaniline to provide the title compound **1h** as a colorless oil (1.08 g, 4.5 mmol, 45% total yield). IR (neat, cm^{-1}) 3418, 2954, 2926, 2868, 1727, 1597, 1491, 1467, 1384, 1366, 1319, 1294, 1255, 1237, 1213, 1177, 1093, 813. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 – 7.04 (m, 2H), 6.63 (d, *J* = 8.8 Hz, 2H), 3.03 (s, 1H), 1.63 – 1.55 (m, 2H), 1.47 (tt, *J* = 13.1, 6.6 Hz, 1H), 1.27 (s, 6H), 1.24 – 1.14 (m, 2H), 0.86 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.6, 128.9, 122.7, 117.9, 54.0, 39.3, 33.2, 28.6, 28.4, 22.8. HRMS (ESI) calcd. for $C_{14}H_{23}NCl$ $[M+H]^+$ *m/z* 240.1519, found 240.1518.

***N*-(2,5-dimethylhexan-2-yl)-3-methylaniline (1i)**



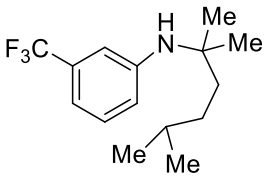
Prepared according to general procedure (A) from *m*-toluidine to provide the title compound **1i** as a colorless oil (0.99 g, 4.5 mmol, 45% total yield). IR (neat, cm^{-1}) 2953, 2923, 2868, 1712, 1605, 1590, 1515, 1486, 1462, 1378, 1366, 1328, 1262, 1184, 1168, 1082, 1021, 766, 692. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (t, *J* = 7.6 Hz, 1H), 6.61 – 6.49 (m, 3H), 2.87 (s, 1H), 2.27 (s, 3H), 1.65 – 1.58 (m, 2H), 1.49 (dt, *J* = 13.2, 6.6 Hz, 1H), 1.28 (s, 6H), 1.27 – 1.19 (m, 2H), 0.88 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.0, 138.7, 128.9, 119.0, 118.0, 114.0, 53.8, 39.8, 33.2, 28.6, 28.4, 22.8, 21.8. HRMS (ESI) calcd. for $C_{15}H_{26}N$ $[M+H]^+$ *m/z* 220.2065, found 220.2065.

3-chloro-*N*-(2,5-dimethylhexan-2-yl)aniline (1j)



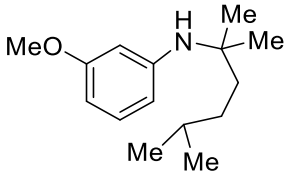
Prepared according to general procedure (A) from 3-chloroaniline to provide the title compound **1j** as a colorless oil (1.29 g, 5.4 mmol, 54% total yield). IR (neat, cm^{-1}) 3424, 2955, 2928, 2868, 1593, 1505, 1480, 1384, 1366, 1327, 1237, 1214, 1166, 1096, 1076, 992, 838, 759, 682. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 (t, *J* = 8.0 Hz, 1H), 6.72 – 6.61 (m, 2H), 6.55 (dd, *J* = 8.2, 1.7 Hz, 1H), 1.66 – 1.58 (m, 2H), 1.49 (dp, *J* = 13.2, 6.6 Hz, 1H), 1.30 (s, 6H), 1.25 – 1.15 (m, 2H), 0.87 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.3, 134.7, 130.0, 117.3, 115.6, 114.2, 53.9, 39.3, 33.1, 28.5, 28.3, 22.8. HRMS (ESI) calcd. for $C_{14}H_{23}NCl$ $[M+H]^+$ *m/z* 240.1519, found 240.1520.

***N*-(2,5-dimethylhexan-2-yl)-3-(trifluoromethyl)aniline (1k)**



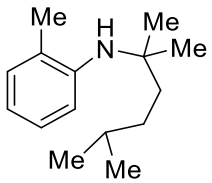
Prepared according to general procedure (A) from 3-(trifluoromethyl)aniline to provide the title compound **1k** as a yellow oil (0.93 g, 3.4 mmol, 34% total yield). IR (neat, cm^{-1}) 2957, 2871, 1612, 1594, 1522, 1482, 1469, 1433, 1386, 1344, 1317, 1285, 1258, 1217, 1160, 1118, 1098, 1070, 998, 859, 781, 697, 659. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (t, *J* = 7.9 Hz, 1H), 6.95 – 6.86 (m, 2H), 6.83 (d, *J* = 8.2 Hz, 1H), 1.69 – 1.60 (m, 2H), 1.49 (dp, *J* = 13.3, 6.6 Hz, 1H), 1.32 (s, 5H), 1.26 – 1.17 (m, 3H), 0.87 (d, *J* = 6.6 Hz, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.3, 131.36 (q, *J* = 31.8 Hz), 129.4, 124.48 (q, *J* = 272.3 Hz), 118.7, 113.75 (q, *J* = 3.8 Hz), 112.10 (q, *J* = 3.8 Hz), 53.9, 39.2, 33.1, 28.5, 28.3, 22.7. HRMS (ESI) calcd. for $C_{15}H_{23}NF_3$ $[M+H]^+$ *m/z* 274.1783, found 274.1780.

***N*-(2,5-dimethylhexan-2-yl)-3-methoxyaniline (1m)**



Prepared according to general procedure (A) from 3-methoxyaniline to provide the title compound **1m** as a yellow oil (0.92 g, 3.9 mmol, 39% total yield). IR (neat, cm^{-1}) 3405, 2953, 2930, 2868, 1610, 1594, 1514, 1492, 1464, 1384, 1366, 1344, 1306, 1265, 1206, 1159, 1116, 1082, 1051, 999, 831, 752, 687. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 – 7.00 (m, 1H), 6.35 – 6.24 (m, 3H), 3.77 (s, 3H), 3.12 (s, 1H), 1.70 – 1.57 (m, 2H), 1.47 (tq, *J* = 11.3, 5.7, 4.9 Hz, 1H), 1.29 (s, 6H), 1.26 – 1.18 (m, 2H), 0.87 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.5, 148.3, 129.7, 109.7, 102.7, 102.5, 55.2, 53.8, 39.5, 33.2, 28.6, 28.4, 22.8. HRMS (ESI) calcd. for $C_{15}H_{26}NO$ $[M+H]^+$ *m/z* 236.2014, found 236.2011.

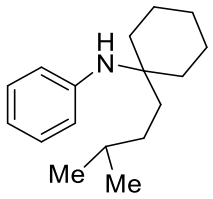
***N*-(2,5-dimethylhexan-2-yl)-2-methylaniline (1n)**



Prepared according to general procedure (A) from *o*-toluidine to provide the title compound **1n** as a colorless oil (0.22 g, 1.0 mmol, 10% total yield). IR (neat, cm^{-1}) 3444, 2955, 2929, 2868, 1606, 1586, 1514, 1481, 1467, 1443, 1384, 1366, 1318, 1261, 1220, 1177, 1119, 1053, 987, 740, 716. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 – 7.02 (m, 2H), 6.86 (d, *J* = 7.9 Hz, 1H), 6.63 (t, *J* = 7.3 Hz, 1H), 3.01 (s, 1H), 2.13 (s, 3H), 1.75 – 1.63 (m, 2H), 1.49 (dp, *J* = 12.9, 6.5 Hz, 1H), 1.34 (s, 6H), 1.26 – 1.15 (m, 2H), 0.87 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ

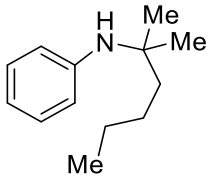
145.1, 130.5, 126.7, 123.2, 116.7, 113.6, 53.59, 39.6, 33.2, 28.6, 28.5, 22.8, 18.3. HRMS (ESI) calcd. for $C_{15}H_{26}N$ $[M+H]^+$ *m/z* 220.2065, found 220.2065.

***N*-(1-isopentylcyclohexyl)aniline (1t)**



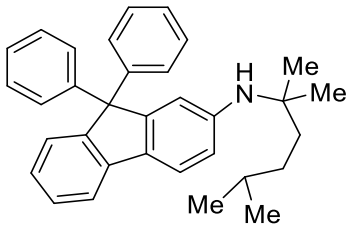
Prepared according to general procedure (A) from cyclohexanone and aniline to provide the title compound **1t** as a colorless oil (1.32 g, 5.4 mmol, 54% total yield). IR (neat, cm^{-1}) 3425, 2926, 2854, 1599, 1496, 1462, 1428, 1383, 1365, 1320, 1279, 1253, 1172, 1120, 1080, 1041, 998, 925, 898, 865, 743, 690. ^1H NMR (400 MHz, $CDCl_3$) δ 7.21 – 7.04 (m, 2H), 6.77 – 6.59 (m, 3H), 3.26 (s, 1H), 1.77 – 1.97 (m, 2H), 1.72 – 1.61 (m, 2H), 1.61 – 1.25 (m, 9H), 1.25 – 1.13 (m, 2H), 0.84 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.0, 129.0, 117.3, 116.1, 55.4, 36.8, 36.4, 32.0, 28.5, 26.2, 22.8, 22.0. HRMS (ESI) calcd. for $C_{17}H_{28}N$ $[M+H]^+$ *m/z* 246.2222, found 246.2221.

***N*-(2-methylhexan-2-yl)aniline (1u)**



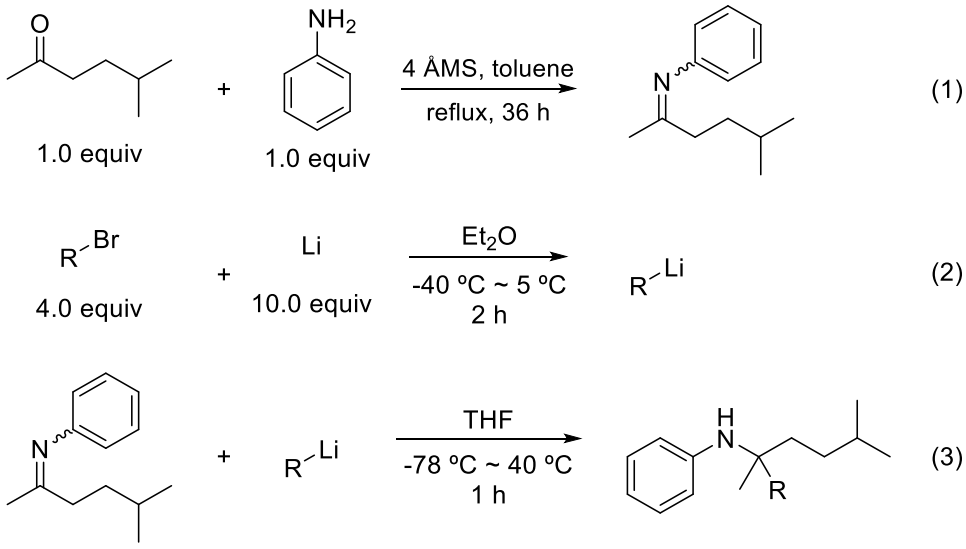
Prepared according to general procedure (A) from hexan-2-one and aniline to provide the title compound **1u** as a colorless oil (0.96 g, 5.0 mmol, 50% total yield). IR (neat, cm^{-1}) 3413, 2957, 2930, 2860, 1600, 1496, 1467, 1427, 1383, 1365, 1321, 1258, 1234, 1215, 1178, 1098, 1080, 1031, 995, 867, 805, 744, 691. ^1H NMR (400 MHz, $CDCl_3$) δ 7.14 (ddd, *J* = 8.1, 6.2, 2.8 Hz, 2H), 6.76 – 6.67 (m, 3H), 3.45 (s, 1H), 1.66 – 1.57 (m, 2H), 1.47 (dq, *J* = 13.1, 6.6 Hz, 1H), 1.28 (s, 6H), 1.26 – 1.18 (m, 2H), 0.86 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.1, 129.0, 118.0, 117.0, 53.9, 39.7, 33.2, 28.6, 28.5, 22.8. HRMS (ESI) calcd. for $C_{13}H_{22}N$ $[M+H]^+$ *m/z* 192.1752, found 192.1752.

***N*-(2,5-dimethylhexan-2-yl)-9,9-diphenyl-9*H*-fluoren-2-amine (1ab)**



Prepared according to general procedure (A) from 9,9-diphenyl-9H-fluoren-2-amine to provide the title compound **1ab** as a off-white solid (2.49 g, 5.6 mmol, 56% total yield). m.p.: 135 – 137 °C. IR (neat, cm^{-1}) 3416, 2957, 2860, 1610, 1582, 1519, 1490, 1458, 1413, 1383, 1351, 1321, 1292, 1235, 1216, 1163, 1117, 1098, 1079, 1030, 851, 813, 781, 756, 726, 697, 657, 635,

620, 599, 552, 479, 440. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.5 Hz, 1H), 7.53 (d, *J* = 8.2 Hz, 1H), 7.34 (d, *J* = 7.6 Hz, 1H), 7.31 – 7.26 (m, 1H), 7.25 – 7.16 (m, 10H), 7.17 – 7.11 (m, 1H), 6.75 (d, *J* = 2.0 Hz, 1H), 6.71 (dd, *J* = 8.2, 2.1 Hz, 1H), 1.61 – 1.51 (m, 2H), 1.39 (dp, *J* = 13.2, 6.6 Hz, 1H), 1.24 (s, 6H), 1.20 – 1.12 (m, 2H), 0.80 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.6, 150.4, 147.1, 146.6, 141.0, 130.5, 128.4, 128.2, 127.4, 126.5, 126.0, 125.9, 120.7, 118.9, 116.6, 114.4, 65.5, 54.1, 39.1, 33.2, 28.6, 28.5, 22.8. HRMS (ESI) calcd. for $C_{33}H_{36}N$ $[M+H]^+$ *m/z* 446.2848, found 446.2848.



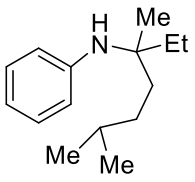
Genaral procedure (B) for the synthesis of substrates.

Step 1: Preparation of imines. The imines were prepared according to *Step 1* of general procedure (A).

Step 2: Preparation of lithium reagents. The bromide (4.0 equiv) in Et_2O (4.0 M) was added dropwise to a vigorously stirred suspension of lithium rods (10.0 equiv) in Et_2O (4.0 M) at -40 °C under N_2 atmosphere. And the mixture was allowed to warm up to 5 °C and stirred for 2 h. The resulting blackish suspension was then used imediately.

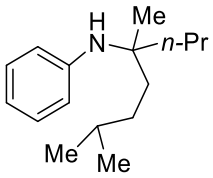
Step 3: Preparation of the substates. The freshly prepared lithium reagent was added dropwise to a vigorously stirred solution of imine in THF (0.1 M) at -78 °C under N_2 atmosphere and then stirred at 40°C for 1 h. After completion, the reaction was quenched with water. The resulting aqueous layer was extracted with EtOAc for 3 times and the combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated under vacuum. The crude material was purified by column chromatography on silica gel to give the substrate **1**.

***N*-(3,6-dimethylheptan-3-yl)aniline (1o)**



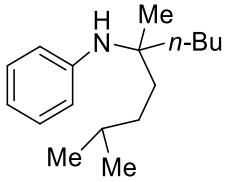
Prepared according to general procedure (B) from bromoethane to provide the title compound **1o** as a colorless oil (0.99 g, 4.5 mmol, 45% total yield). IR (neat, cm^{-1}) 3416, 2955, 2932, 2869, 1599, 1496, 1464, 1429, 1378, 1366, 1320, 1255, 1203, 1177, 1115, 1081, 1032, 994, 867, 743, 691. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (t, *J* = 7.9 Hz, 2H), 6.75 – 6.66 (m, 3H), 3.25 (s, 1H), 1.78 – 1.42 (m, 5H), 1.25 – 1.15 (m, 5H), 0.93 – 0.83 (m, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.1, 129.0, 117.5, 116.3, 56.3, 37.2, 32.7, 32.0, 28.6, 25.7, 22.8, 8.2. HRMS (ESI) calcd. for $C_{15}H_{26}N$ $[M+H]^+$ *m/z* 220.2065, found 220.2065.

_N_-(4,7-dimethyloctan-4-yl)aniline (1p)



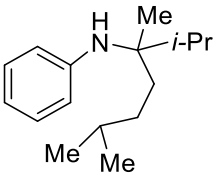
Prepared according to general procedure (B) from 1-bromopropane to provide the title compound **1p** as a colorless oil (0.96 g, 4.1 mmol, 41% total total yield). IR (neat, cm^{-1}) 3416, 2954, 2931, 2869, 1599, 1496, 1467, 1428, 1377, 1366, 1323, 1251, 1177, 1117, 1080, 1033, 994, 866, 743, 691. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 – 7.08 (m, 2H), 6.73 – 6.64 (m, 3H), 1.69 – 1.50 (m, 4H), 1.46 (dq, *J* = 13.2, 6.6 Hz, 1H), 1.34 (ddd, *J* = 11.6, 9.4, 5.4 Hz, 2H), 1.23 (s, 3H), 1.21 – 1.12 (m, 2H), 0.94 – 0.80 (m, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.1, 129.0, 117.5, 116.3, 56.2, 42.4, 37.6, 32.8, 28.6, 26.3, 22.8, 17.0, 14.8. HRMS (ESI) calcd. for $C_{16}H_{28}N$ $[M+H]^+$ *m/z* 234.2222, found 234.2222.

_N_-(2,5-dimethylnonan-5-yl)aniline (1q)



Prepared according to general procedure (B) from 1-bromobutane to provide the title compound **1q** as a colorless oil (1.06 g, 4.3 mmol, 43% total yield). IR (neat, cm^{-1}) 2954, 2929, 2868, 1600, 1497, 1467, 1377, 1323, 1256, 1178, 1080, 1034, 994, 866, 743, 691. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 – 7.08 (m, 2H), 6.73 – 6.65 (m, 3H), 3.17 (s, 1H), 1.69 – 1.51 (m, 4H), 1.47 (dt, *J* = 13.2, 6.6 Hz, 1H), 1.34 – 1.26 (m, 4H), 1.26 – 1.15 (m, 5H), 0.92 – 0.82 (m, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.1, 129.0, 117.5, 116.3, 56.1, 39.6, 37.5, 32.8, 28.6, 26.2, 26.0, 23.3, 22.8, 14.3. HRMS (ESI) calcd. for $C_{17}H_{30}N$ $[M+H]^+$ *m/z* 248.2378, found 248.2379.

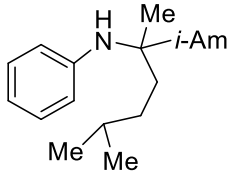
_N_-(2,3,6-trimethylheptan-3-yl)aniline (1r)



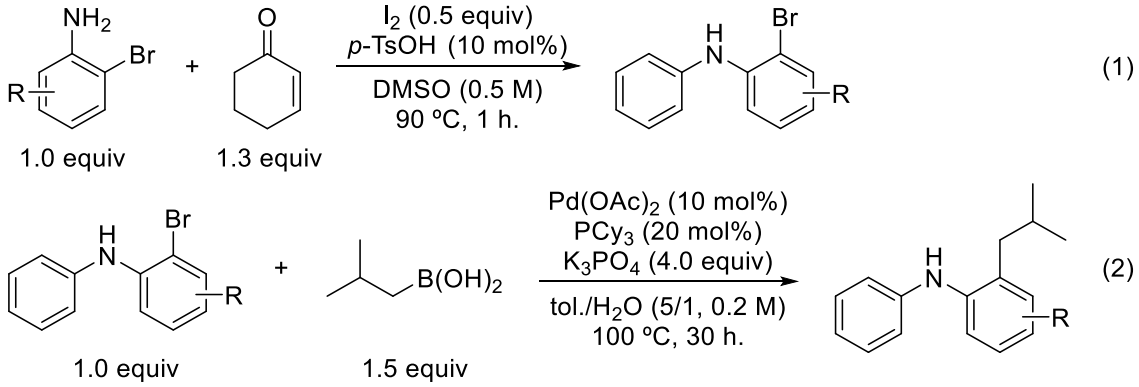
Prepared according to general procedure (B) from 3-methylbutan-2-one and 1-bromo-3-

methylbutane to provide the title compound **1r** as a colorless oil (0.54 g, 2.3 mmol, 23% total yield). IR (neat, cm^{-1}) 3417, 2954, 2870, 1599, 1496, 1467, 1430, 1387, 1366, 1311, 1256, 1230, 1173, 1101, 1033, 994, 867, 744, 690. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 – 7.08 (m, 2H), 6.72 – 6.63 (m, 3H), 3.45 (s, 1H), 2.18 (p, *J* = 6.8 Hz, 1H), 1.79 – 1.67 (m, 1H), 1.66 – 1.54 (m, 1H), 1.46 (dh, *J* = 13.2, 6.6 Hz, 1H), 1.30 – 1.18 (m, 2H), 1.14 (s, 3H), 1.01 – 0.77 (m, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.2, 129.1, 117.2, 116.0, 58.8, 35.1, 34.5, 32.6, 28.7, 22.9, 22.8, 21.8, 17.8, 17.3. HRMS (ESI) calcd. for $C_{16}H_{28}N$ $[M+H]^+$ *m/z* 234.2222, found 234.2222.

***N*-(2,5,8-trimethylnonan-5-yl)aniline (1s)**



Prepared according to general procedure (B) from 1-bromo-3-methylbutane to provide the title compound **1s** as a colorless oil (1.10 g, 4.2 mmol, 42% total yield). IR (neat, cm^{-1}) 2952, 2929, 2868, 1600, 1497, 1467, 1428, 1377, 1366, 1322, 1271, 1256, 1172, 1105, 1080, 1040, 995, 866, 743, 691. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.18 – 7.09 (m, 2H), 6.73 – 6.65 (m, 3H), 3.03 (s, 1H), 1.70 – 1.51 (m, 4H), 1.46 (dq, *J* = 13.2, 6.6 Hz, 2H), 1.27 – 1.14 (m, 7H), 0.87 (dd, *J* = 6.6, 2.2 Hz, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.1, 129.0, 117.5, 116.4, 56.1, 37.5, 32.8, 28.6, 26.3, 22.8. HRMS (ESI) calcd. for $C_{18}H_{32}N$ $[M+H]^+$ *m/z* 262.2535, found 262.2537.



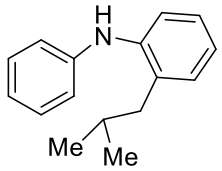
Genaral procedure (C) for the synthesis of substrates.

Step 1: Preparation of Diphenylamines. The diphenylamines were prepared according to a method developed by Barros *et al*.[1] A solution of 2-cyclohexenone, amine, iodine and *p*-TsOH in DMSO was heated at 90 °C for 1 h. After completion, the reaction was cooled to rt and DCM was added. The solution was washed with 20% $Na_2S_2O_3$ followed by brine. The organic layer was dried over Na_2SO_4 and concentrated under vacuum. The crude was purified by column chromatography on silica gel to give the diphenylamine.

Step 2: Preparation of the substates. To a mixture of diphenylamine, isobutylboronic acid , K_3PO_4 and PCy_3 in toluene/H_2O was added $Pd(OAc)_2$ under N_2. The reaction was then heated

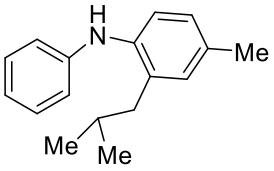
at 100 °C for 30 h. After completion, it was allowed to cool to rt and washed with water. The aqueous layer was extracted with EtOAc for 3 times and the combined organic layer was washed with brine, dried over Na_2SO_4. After concentrated under vaccum, the crude material was purified by column chromatography on silica gel to provide the substrate **1**.

2-isobutyl-*N*-phenylaniline (1v)



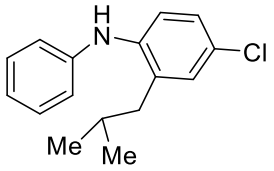
Prepared according to general procedure (C) from 2-bromoaniline to provide the title compound **1v** as a yellow oil (1.53 g, 6.8 mmol, 68% total yield). IR (neat, cm^{-1}) 3390, 2953, 2924, 2866, 1594, 1579, 1496, 1456, 1415, 1383, 1365, 1297, 1174, 1123, 1078, 1027, 995, 890, 812, 743, 692. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.24 (m, 3H), 7.22 – 7.14 (m, 2H), 7.00 (td, *J* = 7.5, 1.2 Hz, 1H), 6.99 – 6.94 (m, 2H), 6.91 (t, *J* = 7.3 Hz, 1H), 5.44 (s, 1H), 2.52 (d, *J* = 7.2 Hz, 2H), 1.96 (dp, *J* = 13.6, 6.7 Hz, 1H), 0.98 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.7, 141.0, 132.6, 131.3, 129.4, 126.8, 122.3, 120.4, 120.2, 117.1, 41.0, 28.9, 22.8. HRMS (ESI) calcd. for $C_{16}H_{20}N$ $[M+H]^+$ *m/z* 226.1596, found 226.1601.

2-isobutyl-4-methyl-*N*-phenylaniline (1w)



Prepared according to general procedure (C) from 2-bromo-4-methylaniline to provide the title compound **1w** as a yellow oil (1.36 g, 5.7 mmol, 57% total yield). IR (neat, cm^{-1}) 3389, 2952, 2922, 2866, 1597, 1495, 1463, 1407, 1382, 1365, 1307, 1226, 1176, 1128, 1077, 1027, 994, 887, 804, 744, 691. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.18 (m, 3H), 7.06 – 6.99 (m, 2H), 6.92 – 6.83 (m, 3H), 5.33 (s, 1H), 2.49 (d, *J* = 7.2 Hz, 2H), 2.36 (s, 3H), 1.93 (hept, *J* = 6.8 Hz, 1H), 0.97 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.7, 138.1, 134.1, 132.5, 131.9, 129.3, 127.4, 122.3, 119.4, 116.0, 40.9, 29.2, 22.8, 21.0. HRMS (ESI) calcd. for $C_{17}H_{22}N$ $[M+H]^+$ *m/z* 240.1752, found 240.1757.

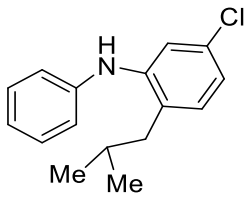
4-chloro-2-isobutyl-*N*-phenylaniline (1x)



Prepared according to general procedure (C) from 2-bromo-4-chloroaniline to provide the title compound **1x** as a colorless oil (1.94 g, 7.5 mmol, 75% total yield). IR (neat, cm^{-1}) 3381, 2957, 2923, 2866, 1593, 1508, 1487, 1434, 1383, 1362, 1337, 1276, 1258, 1209, 1165, 1131, 1115,

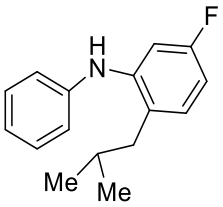
1087, 1053, 978, 933, 904, 812, 748, 693. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (t, *J* = 7.9 Hz, 2H), 7.31 – 7.24 (m, 2H), 7.20 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.07 – 6.99 (m, 3H), 5.45 (s, 1H), 2.56 (d, *J* = 7.3 Hz, 2H), 2.03 (dp, *J* = 13.7, 7.0 Hz, 1H), 1.06 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2, 139.7, 134.4, 130.8, 129.5, 127.0, 126.8, 121.5, 120.7, 117.3, 40.7, 28.8, 22.7. HRMS (ESI) calcd. for $C_{16}H_{19}NCl$ $[M+H]^+$ *m/z* 260.1206, found 260.1208.

5-chloro-2-isobutyl-*N*-phenylaniline (1y)



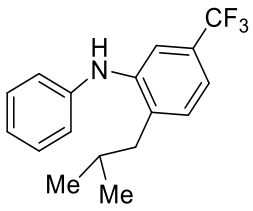
Prepared according to general procedure (C) from 2-bromo-5-chloroaniline to provide the title compound **1y** as a yellow oil (1.86 g, 7.2 mmol, 72% total yield). IR (neat, cm^{-1}) 3425, 2953, 2924, 2867, 1590, 1572, 1496, 1475, 1405, 1384, 1366, 1308, 1269, 1176, 1129, 1077, 1027, 923, 863, 827, 787, 747, 692, 667. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.28 (m, 2H), 7.24 (d, *J* = 2.1 Hz, 1H), 7.07 (d, *J* = 8.1 Hz, 1H), 7.00 (dd, *J* = 16.5, 7.9 Hz, 3H), 6.90 (dd, *J* = 8.1, 2.1 Hz, 1H), 5.45 (s, 1H), 2.46 (d, *J* = 7.3 Hz, 2H), 1.93 (hept, *J* = 6.8 Hz, 1H), 0.97 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.1, 142.6, 132.2, 132.1, 129.6, 129.3, 121.6, 121.3, 118.6, 118.2, 40.5, 28.6, 22.7. HRMS (ESI) calcd. for $C_{16}H_{19}NCl$ $[M+H]^+$ *m/z* 260.1206, found 260.1210.

5-fluoro-2-isobutyl-*N*-phenylaniline (1z)



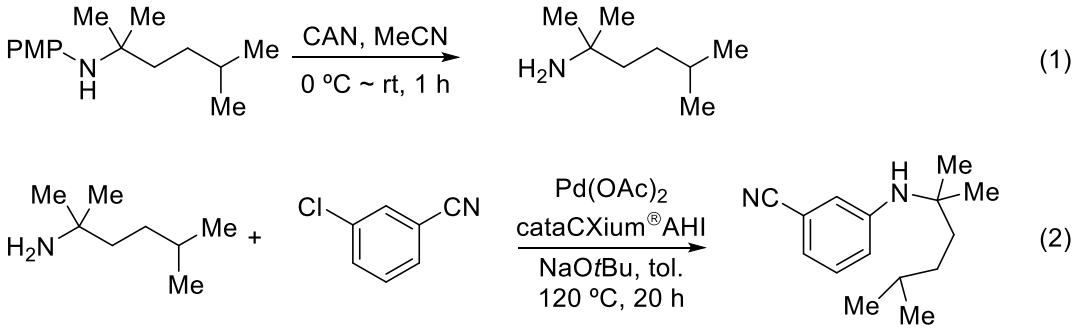
Prepared according to general procedure (C) from 2-bromo-5-fluoroaniline to provide the title compound **1z** as a colorless oil (1.87 g, 7.7 mmol, 77% total yield). IR (neat, cm^{-1}) 3437, 2954, 2925, 2867, 1595, 1512, 1496, 1464, 1430, 1417, 1384, 1366, 1310, 1278, 1240, 1157, 1109, 1078, 1027, 986, 850, 787, 742, 692. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, 2H), 7.13 – 7.03 (m, 3H), 7.03 – 6.94 (m, 2H), 6.63 (td, *J* = 8.3, 2.6 Hz, 1H), 5.52 (s, 1H), 2.47 (d, *J* = 7.3 Hz, 2H), 1.93 (hept, *J* = 6.8 Hz, 1H), 0.98 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.0 (d, *J* = 242.3 Hz), 143.0, 142.9 (d, *J* = 10.1 Hz), 132.1 (d, *J* = 9.4 Hz), 129.6, 126.0, 125.9, 121.7, 118.8, 107.6 (d, *J* = 21.1 Hz), 104.7 (d, *J* = 24.7 Hz), 40.4, 28.7, 22.7. HRMS (ESI) calcd. for $C_{16}H_{19}NF$ $[M+H]^+$ *m/z* 244.1502, found 244.1508.

2-isobutyl-*N*-phenyl-5-(trifluoromethyl)aniline (1aa)



Prepared according to general procedure (C) from 2-bromo-5-(trifluoromethyl)aniline to provide the title compound **1aa** as a colorless oil (2.73 g, 8.1 mmol, 81% total yield). IR (neat, cm^{-1}) 3440, 2957, 2870, 1598, 1582, 1520, 1497, 1467, 1431, 1419, 1329, 1271, 1222, 1162, 1115, 1073, 933, 878, 835, 804, 744, 693. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (s, 1H), 7.36 – 7.29 (m, 2H), 7.26 (d, *J* = 7.9 Hz, 1H), 7.19 (d, *J* = 7.9 Hz, 1H), 7.02 (dd, *J* = 11.7, 7.6 Hz, 3H), 5.54 (s, 1H), 2.55 (d, *J* = 7.3 Hz, 2H), 1.99 (dp, *J* = 13.6, 6.7 Hz, 1H), 1.00 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.1, 141.9, 134.8, 131.6, 129.7, 129.3 (q, *J* = 32.2 Hz), 124.4 (q, *J* = 272.1 Hz), 121.7, 118.5, 117.9 (q, *J* = 3.8 Hz), 115.0 (q, *J* = 3.8 Hz), 40.9, 28.6, 22.8. HRMS (ESI) calcd. for $C_{17}H_{19}NF_3$ $[M+H]^+$ *m/z* 294.1470, found 294.1481.

3-((2,5-dimethylhexan-2-yl)amino)benzonitrile (1l)



Step 1: Preparation of 2,5-dimethylhexan-2-amine. Ceric ammonium nitrate (2.5 equiv) in MeCN (0.1 M) was added to a solution of *N*-(2,5-dimethylhexan-2-yl)-4-methoxyaniline (1.0 equiv) in MeCN (0.05 M) dropwise at 0 °C and stirred at rt for 1 h. After completion, water and Et_2O were added, the layers were separated and the aqueous layer was washed with Et_2O. The aqueous layer was basified with sodium carbonate to pH 10 and extracted with Et_2O. The combined organic layer was then acidized with 2N HCl and washed with water. The combined aqueous layer was again basified with sodium carbonate to pH 10 and extracted with Et_2O and the combined organic layer was dried over Na_2SO_4 and concentrated to give the 2,5-dimethylhexan-2-amine as a light yellow oil (2.45 g, 19.0 mmol, 19%).

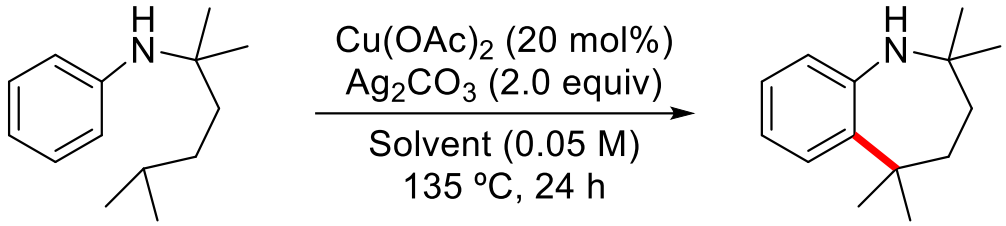
*Step 2: Preparation of 3-((2,5-dimethylhexan-2-yl)amino)benzonitrile (**1l**).* **1l** was prepared according to the method developped by Beller *et al*[2]. To a 25 mL pressure tube was added $Pd(OAc)_2$ (0.005 equiv), di(1-adamantyl)-*N*-butylphosphine hydroiodide (0.01 equiv), and NaO*t*Bu (1.2 equiv) and was purged with argon. Toluene (1.0 M), 3-chlorobenzonitrile (1.0 equiv) and 2,5-dimethylhexan-2-amine (1.2 equiv) were added successively. The mixture was stirred at 120 °C for 20 h. After cooling to rt, the mixture was diluted with diethyl ether and washed with water. The organic phase was dried over Na_2SO_4 and concentrated. The crude was purified by column chromatography on silica gel to provide **1l** as a colorless oil (0.23 g, 1.0 mmol, 50%). IR (neat, cm^{-1}) 3391, 2955, 2930, 2868, 2227, 1599, 1581, 1519, 1483, 1467,

1421, 1385, 1367, 1338, 1303, 1238, 1217, 1174, 1116, 1079, 1004, 850, 777, 683. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (t, *J* = 7.9 Hz, 1H), 6.92 (d, *J* = 7.4 Hz, 1H), 6.89 (s, 1H), 6.83 (d, *J* = 8.3 Hz, 1H), 3.73 (s, 1H), 1.70 – 1.55 (m, 2H), 1.53 – 1.40 (m, 1H), 1.31 (s, 6H), 1.23 – 1.11 (m, 2H), 0.86 (s, 3H), 0.85 (s, 3H).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.4, 129.8, 120.6, 120.0, 119.7, 117.6, 112.8, 53.9, 39.0, 33.1, 28. 5, 28.2, 22.8. HRMS (ESI) calcd. for $C_{15}H_{23}N_2$ $[M+H]^+$ *m/z* 231.1861, found 231.1854.

III. Novel and Facile Synthesis of 1-Benzazepines via Copper-Catalyzed Oxidative C(sp^3)-H/C(sp^2)-H Cross-Coupling

Reaction Optimization

Table S1 | Solvent Screening

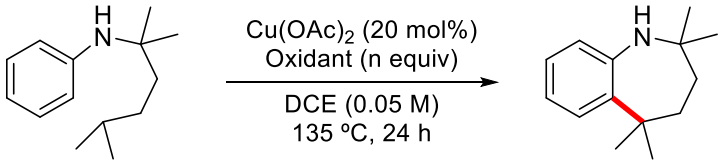


1a **2a**

entry	Solvent	yield[a]	entry	Solvent	yield[a]
1	DCE	19 (20[b])	2	$PhCH_3$	6
3	$PhCF_3$	19	4	*m*-xylene	0
5	*o*-xylene	0	6	mesitylene	0
7	*p*-xylene	0	8	CH_2Cl_2	13
9	PhCl	0	10	1,1,2,2-TeCE	0
11	$CHCl_3$	3	12	DMSO	0
13	1,1,1-TrCE	3	14	1,4-dioxane	13
15	DMF	2	16	MeCN	14
17	THF	8	18	PrOH	3
19	Acetone	11	20	PE	25
21	$MeNO_2$	1	22	1-Bromobutane	4
23	MeOH	2	24	DME	22
25	1,2-DBE	0	26	*i*-PrOH	11
27	MTBE	9	28	ME	0
29	EA	3	30	*i*-BuOH	7
31	EtOH	6	32	*t*-BuOH	21
33	BuOH	2	34	TFE	0
35	*t*-AmOH	13	36	HFIP	0

[a]Determined by GC.[b]Isolated yield.

Table S2 | Oxidant Screening

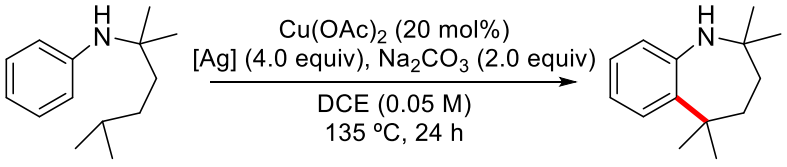


1a **2a**

entry	Oxidant (equiv)	yield[a]	entry	Oxidant (equiv)	yield[a]
1	$K_2S_2O_8$ (2.0)	0	2	TEMPO (4.0)	0
3	BPO (2.0)	0	4	PIDA (2.0)	0
5	AgOAc (4.0)	7	6	*t*-BuOOH (2.0)	0
7	O_2 (1 atm)	0	8	*t*-BuOO*t*-Bu (2.0)	6
9	Oxone (2.0)	0	10	NFSI (2.0)	0
11	$AgNO_3$ (4.0)	0	12	BQ (2.0)	0
13	DDQ (2.0)	0	14	AgTFA (4.0)	0
15	PivOAg (4.0)	0	16	*n*-C_6H_{11}COOAg (4.0)	0
17	AgOTf (4.0)	0	18	Ag_2O (2.0)	48
19	AgF (4.0)	0	20	AgOTs (4.0)	0
21	$AgClO_4$ (4.0)	0	22	$AgNO_2$ (4.0)	0
23	AgMes (4.0)	0	24	$(NH_4)_2S_2O_8$ (2.0)	0
25	$Na_2S_2O_8$ (2.0)	0	26	$Ce(SO_4)_2$ (4.0)	0
27	CAN (4.0)	0	28	$FeCl_3$ (4.0)	0
29	$FeBr_3$ (4.0)	0	30	FeF_3 (4.0)	0
31	$Fe(NO_3)_3$ (4.0)	0	32	$Fe_2(SO_4)_3$ (4.0)	0
33	$Cu(OAc)_2$ (4.0)	0	34	AgOAc (4.0) Na_2CO_3 (4.0)	44

[a]Determined by GC.

Table S3 | Ag salts Screening

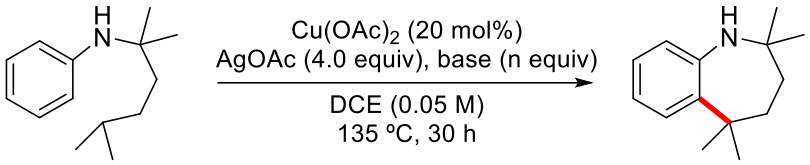


1a **2a**

entry	[Ag]	yield[a]	entry	[Ag]	yield[a]
1	AgF	12	2	$AgNO_3$	0
3	$AgNO_2$	0	4	AgOTs	0
5	$AgClO_4$	0	6	AgTFA	0
7	AgOTf	0			

[a]Determined by GC.

Table S4 | Base Screening

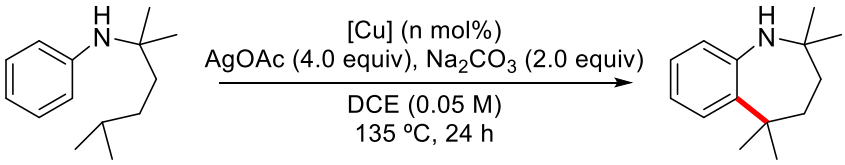


1a **2a**

entry	base (equiv)	yield[a]	entry	base (equiv)	yield[a]
1	Na_2CO_3 (2.0)	61	2	Li_2CO_3 (2.0)	20
3	K_2CO_3 (2.0)	41	4	Cs_2CO_3 (2.0)	46
5	$NaHCO_3$ (4.0)	57	6	$KHCO_3$ (4.0)	55
7	K_3PO_4 (1.3)	43	8	KF (4.0)	53

[a]Determined by GC.

Table S5 | Cu salts Screening

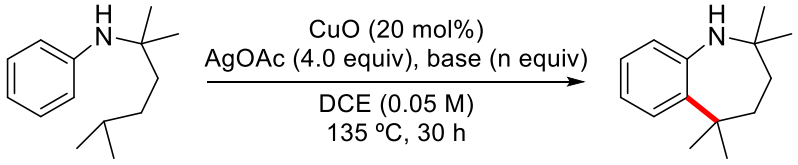


1a **2a**

entry	[Cu] (n mol%)	yield[a]	entry	[Cu] (n mol%)	yield[a]
1	Cu (20)	54	2	Cu_2O (10)	34
3	$Cu_2(OH)_2CO_3$ (10)	61	4	$CuCO_3$ (20)	61
5	CuCN (20)	62	6	CuO (20)	70

[a]Determined by GC.

Table S6 | Re-screening of Base

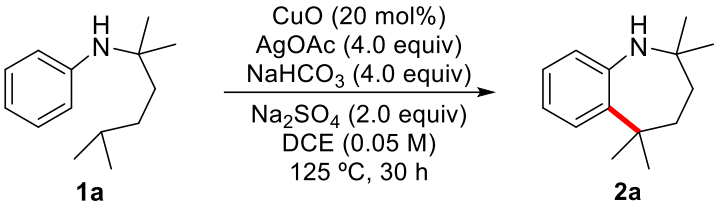


1a **2a**

entry	base (equiv)	yield[a]	entry	base (equiv)	yield[a]
1	Na_2CO_3 (2.0)	77	2	Li_2CO_3 (2.0)	52
3	K_2CO_3 (2.0)	71	4	Cs_2CO_3 (2.0)	45
5	$NaHCO_3$ (4.0)	85	6	$KHCO_3$ (4.0)	74
7	K_3PO_4 (1.3)	50	8	KF (4.0)	71
9	NaOAc (4.0)	61			

[a]Determined by GC.

Table S7 | Variation of Standard Conditions

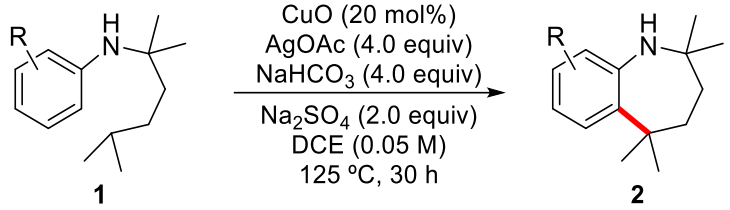


1a **2a**

entry	variation	yield[a]
1	10% CuO	79
2	300% AgOAc, 300% $NaHCO_3$	89
3	250% AgOAc, 250% $NaHCO_3$	70
4	100% Na_2SO_4	86
5	1 mL DCE	83
6	4 mL DCE	77
7	110 ºC	8
8	24 h	64

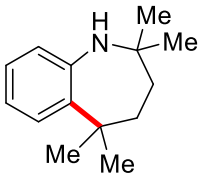
[a]Isolated yield.

Substrate Screening



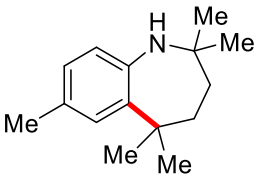
Genaral procedure (D) for the novel and facile synthesis of 1-benzazepines via copper-catalyzed oxidative C(sp^3)-H/C(sp^2)-H cross-coupling. To an oven-dried 35 mL screw-cap sealed tube equipped with a magnetic stir bar was added CuO (20 mol%), AgOAc (4.0 equiv), $NaHCO_3$ (4.0 equiv), Na_2SO_4 (2.0 equiv), substrate **1** (0.3 mmol, 1.0 equiv) and 1,2-dichloroethane (6.0 mL) at air atmosphere. The vessel was then sealed with a Teflon screw-cap, stirred vigorously at rt for 5 min, and placed into a preheated oil bath at 125 °C for 30 h. After completion, the reaction mixture was allowed to cool to room temperature, and was directly filtered through a short pad of silica gel washed with EtOAc. The filtrate was concentrated under vacuum and purified by column chromatography on silica gel to obtain the corresponding product **2**.

2,2,5,5-tetramethyl-2,3,4,5-tetrahydro-1*H*-benzo[*b*]azepine (2a)



Prepared according to general procedure (D) using **1a** to provide the title compound **2a** as a colorless oil (56.6 mg, 0.28 mmol, 93%). IR (neat, cm^{-1}) 2953, 2921, 2852, 1738, 1460, 1377, 1362, 1260, 1237, 1162, 1083, 1053, 1020, 972, 851, 802, 751. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 7.1 Hz, 1H), 7.01 (td, *J* = 7.5, 1.3 Hz, 1H), 6.93 – 6.87 (m, 1H), 6.61 (d, *J* = 7.6 Hz, 1H), 2.74 (s, 1H), 1.83 – 1.69 (m, 2H), 1.69 – 1.60 (m, 2H), 1.37 (s, 4H), 1.12 (s, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.1, 140.0, 126.5, 126.5, 123.1, 121.5, 52.7, 38.2, 38.1, 36.6, 29.4. HRMS (ESI) calcd. for $C_{14}H_{22}N$ $[M+H]^+$ *m/z* 204.1752, found 204.1757.

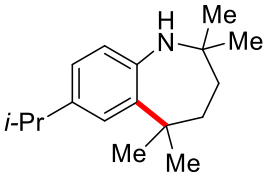
2,2,5,5,7-pentamethyl-2,3,4,5-tetrahydro-1*H*-benzo[*b*]azepine (2b)



Prepared according to general procedure (D) using **1b** to provide the title compound **2b** as a colorless oil (50.1 mg, 0.23 mmol, 77%). IR (neat, cm^{-1}) 2957, 2923, 2854, 1737, 1606, 1479, 1467, 1443, 1382, 1360, 1259, 1241, 1193, 1177, 1162, 1145, 1088, 1020, 806, 675. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (s, 1H), 6.81 (d, *J* = 7.6 Hz, 1H), 6.51 (d, *J* = 7.7 Hz, 1H), 2.27 (s, 3H), 1.80 – 1.67 (m, 2H), 1.67 – 1.58 (m, 2H), 1.36 (s, 6H), 1.10 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 139.9, 130.5, 127.4, 126.9, 123.1, 52.6, 38.2, 38.0, 36.7, 29.0, 21.1. HRMS

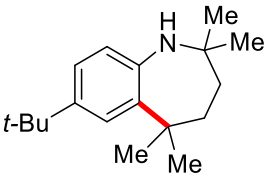
(ESI) calcd. for $C_{15}H_{24}N$ $[M+H]^+$ *m/z* 218.1909, found 218.1912.

7-isopropyl-2,2,5,5-tetramethyl-2,3,4,5-tetrahydro-1*H*-benzo[*b*]azepine (2c)



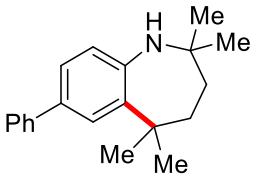
Prepared according to general procedure (D) (but for 25 h.) using **1c** to provide the title compound **2c** as a colorless oil (47.8 mg, 0.20 mmol, 65%). IR (neat, cm^{-1}) 2955, 2927, 2866, 1607, 1504, 1478, 1440, 1383, 1361, 1322, 1269, 1241, 1194, 1177, 1165, 1150, 1103, 1087, 1059, 1019, 945, 910, 887, 823, 775, 736, 690, 667, 639. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (d, *J* = 2.0 Hz, 1H), 6.85 (dd, *J* = 7.9, 2.0 Hz, 1H), 6.53 (d, *J* = 7.8 Hz, 1H), 2.83 (hept, *J* = 6.9 Hz, 1H), 1.83 – 1.67 (m, 2H), 1.67 – 1.57 (m, 2H), 1.37 (s, 6H), 1.22 (d, *J* = 6.9 Hz, 3H), 1.09 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.7, 141.7, 139.8, 125.0, 123.8, 122.9, 52.6, 38.3, 38.2, 36.8, 33.7, 29.3, 24.4. HRMS (ESI) calcd. for $C_{17}H_{28}N$ $[M+H]^+$ *m/z* 246.2222, found 246.2232.

7-(tert-butyl)-2,2,5,5-tetramethyl-2,3,4,5-tetrahydro-1*H*-benzo[*b*]azepine (2d)



Prepared according to general procedure (D) (but with 3 equiv [Ag].) using **1d** to provide the title compound **2d** as a colorless oil (66.0 mg, 0.26 mmol, 85%). IR (neat, cm^{-1}) 2955, 2865, 1606, 1504, 1478, 1440, 1384, 1360, 1268, 1244, 1195, 1177, 1166, 1150, 1088, 1018, 945, 887, 820, 770, 745, 687, 656, 642, 553, 504. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 2.2 Hz, 1H), 6.99 (dd, *J* = 8.0, 2.2 Hz, 1H), 6.52 (d, *J* = 8.0 Hz, 1H), 1.80 – 1.67 (m, 2H), 1.67 – 1.58 (m, 2H), 1.37 (s, 6H), 1.29 (s, 9H), 1.10 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.8, 143.3, 139.3, 123.6, 123.0, 122.5, 52.6, 38.4, 38.3, 36.8, 34.4, 31.8, 29.6. HRMS (ESI) calcd. for $C_{18}H_{30}N$ $[M+H]^+$ *m/z* 260.2378, found 260.2388.

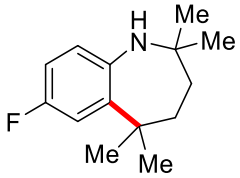
2,2,5,5-tetramethyl-7-phenyl-2,3,4,5-tetrahydro-1*H*-benzo[*b*]azepine (2e)



Prepared according to general procedure (D) using **1e** to provide the title compound **2e** as a colorless oil (71.1 mg, 0.26 mmol, 85%). IR (neat, cm^{-1}) 3342, 2955, 2909, 1600, 1475, 1449, 1437, 1385, 1361, 1277, 1242, 1195, 1177, 1163, 1146, 1104, 1086, 1052, 1018, 944, 889, 826, 806, 754, 696, 609, 585, 554, 511, 495. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.6 Hz, 2H), 7.50 (s, 1H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.25 (dd, *J* = 15.3, 7.2 Hz, 2H), 6.66 (d, *J* = 7.9 Hz, 1H),

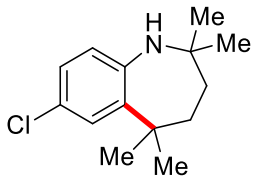
2.78 (s, 1H), 1.86 – 1.71 (m, 2H), 1.71 – 1.62 (m, 2H), 1.41 (s, 6H), 1.13 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.6, 141.8, 140.2, 134.2, 128.7, 126.8, 126.4, 125.7, 125.0, 123.5, 52.9, 38.3, 38.1, 36.7, 29.3. HRMS (ESI) calcd. for $C_{20}H_{26}N$ $[M+H]^+$ *m/z* 280.2065, found 280.2064.

7-fluoro-2,2,5,5-tetramethyl-2,3,4,5-tetrahydro-1*H*-benzo[*b*]azepine (2g)



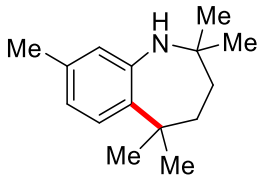
Prepared according to general procedure (D) using **1g** to provide the title compound **2g** as a yellow oil (45.7 mg, 0.21 mmol, 69%). IR (neat, cm^{-1}) 2959, 2927, 2857, 1726, 1592, 1509, 1481, 1468, 1444, 1384, 1364, 1267, 1200, 1175, 1103, 1019, 932, 909, 872, 809. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96 (d, *J* = 11.5 Hz, 1H), 6.68 (t, *J* = 6.9 Hz, 1H), 6.57 – 6.48 (m, 1H), 1.80 – 1.67 (m, 2H), 1.67 – 1.58 (m, 2H), 1.35 (s, 6H), 1.09 (s, 6H).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.35 (d, *J* = 237.2 Hz), 142.02 (d, *J* = 6.1 Hz), 141.91 (d, *J* = 2.0 Hz), 123.53 (d, *J* = 7.9 Hz), 113.43 (d, *J* = 23.1 Hz), 112.25 (d, *J* = 21.7 Hz), 52.4, 38.1, 36.2, 28.7. HRMS (ESI) calcd. for $C_{14}H_{21}NF$ $[M+H]^+$ *m/z* 222.1658, found 222.1666.

7-chloro-2,2,5,5-tetramethyl-2,3,4,5-tetrahydro-1*H*-benzo[*b*]azepine (2h)



Prepared according to general procedure (D) using **1h** to provide the title compound **2h** as a colorless oil (64.7 mg, 0.27 mmol, 91%). IR (neat, cm^{-1}) 3351, 2958, 2915, 1593, 1496, 1477, 1439, 1391, 1362, 1277, 1236, 1194, 1177, 1163, 1138, 1120, 1096, 1084, 1066, 1020, 977, 957, 944, 877, 862, 819, 805, 765, 744, 730, 683, 646, 588, 549, 517, 504. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, *J* = 2.4 Hz, 1H), 6.95 (dd, *J* = 8.2, 2.4 Hz, 1H), 6.53 (d, *J* = 8.2 Hz, 1H), 3.03 (s, 1H), 1.82 – 1.67 (m, 2H), 1.67 – 1.57 (m, 2H), 1.34 (s, 6H), 1.10 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.8, 141.8, 126.8, 126.4, 126.1, 124.1, 52.7, 38.3, 38.0, 36.3, 29.6. HRMS (ESI) calcd. for $C_{14}H_{21}NCl$ $[M+H]^+$ *m/z* 238.1363, found 238.1365.

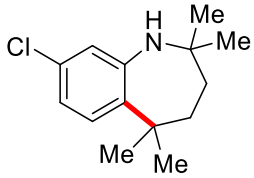
2,2,5,5,8-pentamethyl-2,3,4,5-tetrahydro-1*H*-benzo[*b*]azepine (2i)



Prepared according to general procedure (D) using **1i** to provide the title compound **2i** as a colorless oil (43.0 mg, 0.20 mmol, 66%). IR (neat, cm^{-1}) 2957, 2924, 2855, 1729, 1612, 1509, 1443, 1380, 1363, 1256, 1222, 1199, 1161, 1079, 1019, 953, 859, 803, 733, 695, 627. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (d, *J* = 7.9 Hz, 1H), 6.70 (d, *J* = 7.9 Hz, 1H), 6.43 (s, 1H), 2.23 (s,

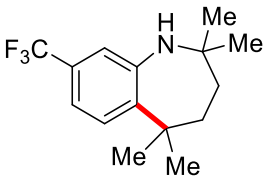
3H), 1.72 (m, 2H), 1.82 – 1.67 (m, 2H), 1.67 – 1.57 (s, 6H), 1.10 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.9, 137.1, 136.0, 126.6, 123.8, 122.2, 52.7, 38.2, 37.8, 36.8, 29.6, 20.7. HRMS (ESI) calcd. for $C_{15}H_{24}N$ $[M+H]^+$ *m/z* 218.1909, found 218.1913.

8-chloro-2,2,5,5-tetramethyl-2,3,4,5-tetrahydro-1*H*-benzo[*b*]azepine (2j)



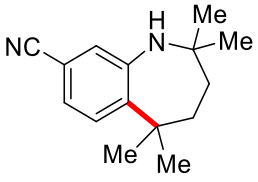
Prepared according to general procedure (D) (but with 140 °C for 25 h.) using **1j** to provide the title compound **2j** as a colorless oil (47.6 mg, 0.20 mmol, 67%). IR (neat, cm^{-1}) 2957, 2923, 2865, 1590, 1573, 1505, 1475, 1441, 1389, 1362, 1290, 1234, 1196, 1162, 1136, 1115, 1101, 1074, 1020, 969, 950, 933, 921, 879, 851, 802, 766, 727, 685, 625, 597, 577, 514. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (d, *J* = 8.4 Hz, 1H), 6.84 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.62 (d, *J* = 2.2 Hz, 1H), 3.07 (s, 1H), 1.81 – 1.67 (m, 2H), 1.67 – 1.57 (m, 2H), 1.33 (s, 6H), 1.11 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.5, 138.6, 131.3, 127.9, 122.4, 121.2, 53.0, 38.0, 36.4, 29.2. HRMS (ESI) calcd. for $C_{14}H_{21}NCl$ $[M+H]^+$ *m/z* 238.1363, found 238.1373.

2,2,5,5-tetramethyl-8-(trifluoromethyl)-2,3,4,5-tetrahydro-1*H*-benzo[*b*]azepine (2k)



Prepared according to general procedure (D) (but with 140 °C for 35 h.) using **1k** to provide the title compound **2k** as a yellow oil (46.3 mg, 0.17 mmol, 57%). IR (neat, cm^{-1}) 2961, 2923, 1614, 1582, 1477, 1443, 1406, 1386, 1365, 1332, 1301, 1269, 1235, 1163, 1139, 1118, 1098, 1069, 1020, 972, 953, 923, 869, 820, 807, 703, 686, 587, 512. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.2 Hz, 1H), 7.15 – 7.07 (m, 1H), 6.87 – 6.83 (m, 1H), 3.23 (s, 1H), 1.85 – 1.67 (m, 2H), 1.67 – 1.59 (m, 2H), 1.37 (s, 6H), 1.12 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.6, 143.8, 128.7 (q, *J* = 32.1 Hz), 127.2, 124.4 (q, *J* = 271.8 Hz), 119.2 (q, *J* = 3.6 Hz), 118.0 (q, *J* = 3.8 Hz), 53.0, 38.5, 37.9, 36.1, 29.3. HRMS (ESI) calcd. for $C_{15}H_{21}NF_3$ $[M+H]^+$ *m/z* 272.1626, found 272.1632.

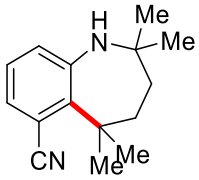
2,2,5,5-tetramethyl-2,3,4,5-tetrahydro-1*H*-benzo[*b*]azepine-8-carbonitrile (2l)



Prepared according to general procedure (D) (but with 140 °C for 45 h.) using **1l** to provide the title compound **2l** as a white solid (11.4 mg, 0.05 mmol, 33%). m.p.: 115 – 117 °C. IR (neat, cm^{-1}) 3335, 2970, 2913, 2227, 1603, 1566, 1531, 1482, 1468, 1449, 1395, 1383, 1365, 1299,

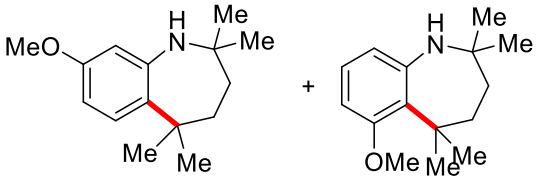
1271, 1238, 1201, 1193, 1160, 1143, 1103, 1076, 1021, 997, 956, 936, 891, 869, 811, 794, 763, 741, 707, 650, 614, 556, 516, 491. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.1 Hz, 1H), 7.15 (d, *J* = 8.0 Hz, 1H), 6.88 (s, 1H), 3.22 (s, 1H), 1.82 – 1.69 (m, 2H), 1.69 – 1.61 (m, 2H), 1.35 (s, 6H), 1.11 (s, 6H).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.0, 145.7, 127.6, 125.6, 125.2, 119.3, 110.1, 53.1, 38.9, 37.7, 35.9, 29.3. HRMS (ESI) calcd. for $C_{15}H_{21}N_2$ $[M+H]^+$ *m/z* 229.1705, found 229.1697.

2,2,5,5-tetramethyl-2,3,4,5-tetrahydro-1*H*-benzo[*b*]azepine-6-carbonitrile (2l')



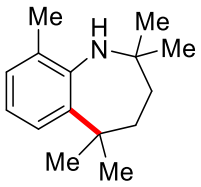
Prepared according to general procedure (D) (but with 140 °C for 45 h.) using **1l** to provide the title compound **2l'** as a white solid (8.5 mg, 0.03 mmol, 15%). m.p.: 104 – 106 °C. IR (neat, cm^{-1}) 3346, 3325, 2952, 2921, 2868, 2218, 1726, 1600, 1574, 1514, 1477, 1447, 1414, 1382, 1362, 1284, 1237, 1182, 1156, 1122, 1108, 1075, 1055, 1022, 999, 956, 936, 875, 840, 810, 749, 725, 703, 644, 622, 587, 520, 481, 464, 438. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 7.6 Hz, 1H), 7.02 (t, *J* = 7.6 Hz, 1H), 6.78 (d, *J* = 7.9 Hz, 1H), 2.84 (s, 1H), 1.78 – 1.51 (m, 10H), 1.14 (s, 6H).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.9, 142.9, 130.9, 128.8, 126.8, 121.6, 113.0, 55.6, 40.6, 38.4, 35.1, 30.2. HRMS (ESI) calcd. for $C_{15}H_{21}N_2$ $[M+H]^+$ *m/z* 229.1705, found 229.1697.

8-methoxy-2,2,5,5-tetramethyl-2,3,4,5-tetrahydro-1*H*-benzo[*b*]azepine (2m) + 6-methoxy-2,2,5,5-tetramethyl-2,3,4,5-tetrahydro-1*H*-benzo[*b*]azepine (2m')



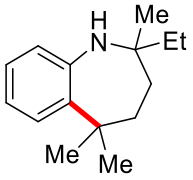
Prepared according to general procedure (D) using **1m** to provide the title compound **2m** and **2m'** as a mixture (**2m**:**2m'**=1.04:1, colorless oil, 44.0 mg, 0.19 mmol, 63%). IR (neat, cm^{-1}) 3346, 2953, 2923, 2865, 1609, 1582, 1502, 1464, 1438, 1382, 1361, 1316, 1289, 1256, 1207, 1161, 1130, 1085, 1064, 1043, 1021, 993, 952, 925, 847, 794, 758, 727, 699, 638. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (d, *J* = 8.6 Hz, 1H), 6.94 (t, *J* = 8.0 Hz, 1.04H), 6.55 (d, *J* = 8.1 Hz, 1.04H), 6.44 (d, *J* = 8.6 Hz, 1H), 6.24 (d, *J* = 7.8 Hz, 1.04H), 6.19 (d, *J* = 1.9 Hz, 1H), 3.79 (s, 3.12H), 3.76 (s, 3H), 1.93 – 1.51 (m, 8.16H), 1.42 (s, 6.24H), 1.35 (s, 6.24H), 1.15 (s, 6H), 1.12 (s, 6H).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.7, 158.0, 147.3, 145.4, 132.8, 127.6, 127.4, 126.5, 117.6, 108.9, 106.7, 105.7, 55.7, 55.4, 55.2, 52.9, 40.0, 39.7, 38.2, 37.5, 36.9, 34.6, 30.7, 29.4. HRMS (ESI) calcd. for $C_{15}H_{24}NO$ $[M+H]^+$ *m/z* 234.1858, found 234.1861.

2,2,5,5,9-pentamethyl-2,3,4,5-tetrahydro-1*H*-benzo[*b*]azepine (2n)



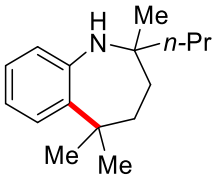
Prepared according to general procedure (D) (but for 35 h.) using **1n** to provide the title compound **2n** as a colorless oil (35.8 mg, 0.17 mmol, 55%). IR (neat, cm^{-1}) 3401, 2956, 2927, 1590, 1471, 1438, 1422, 1385, 1360, 1260, 1247, 1217, 1171, 1161, 1131, 1113, 1090, 1064, 1029, 959, 941, 898, 789, 758, 732, 691, 634, 556. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, *J* = 7.9 Hz, 1H), 7.00 (d, *J* = 7.3 Hz, 1H), 6.81 (t, *J* = 7.6 Hz, 1H), 3.26 (s, 1H), 2.23 (s, 3H), 1.85 – 1.70 (m, 2H), 1.70 – 1.61 (m, 2H), 1.40 (s, 6H), 1.14 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.7, 140.3, 128.4, 128.0, 124.8, 120.7, 52.9, 38.6, 38.3, 36.6, 29.0, 19.3. HRMS (ESI) calcd. for $C_{15}H_{24}N$ $[M+H]^+$ *m/z* 218.1909, found 218.1913.

2-ethyl-2,5,5-trimethyl-2,3,4,5-tetrahydro-1*H*-benzo[*b*]azepine (2o)



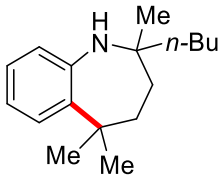
Prepared according to general procedure (D) using **1o** to provide the title compound **2o** as a colorless oil (55.3 mg, 0.26 mmol, 85%). IR (neat, cm^{-1}) 2961, 2928, 1599, 1581, 1470, 1441, 1384, 1358, 1293, 1259, 1237, 1171, 1129, 1089, 1053, 998, 921, 748, 695, 669, 605, 544, 504. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.01 (td, *J* = 7.4, 1.4 Hz, 1H), 6.89 (td, *J* = 7.5, 1.2 Hz, 1H), 6.62 (dd, *J* = 7.7, 1.2 Hz, 1H), 2.87 (s, 1H), 1.87 – 1.69 (m, 2H), 1.69 – 1.60 (m, 2H), 1.48 – 1.39 (m, 2H), 1.37 (d, *J* = 4.9 Hz, 6H), 1.04 (s, 3H), 0.88 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.8, 140.0, 126.6, 126.4, 123.2, 121.3, 55.0, 38.2, 36.2, 35.8, 34.1, 29.0, 26.5, 8.4. HRMS (ESI) calcd. for $C_{15}H_{24}N$ $[M+H]^+$ *m/z* 218.1909, found 218.1915.

2,5,5-trimethyl-2-propyl-2,3,4,5-tetrahydro-1*H*-benzo[*b*]azepine (2p)



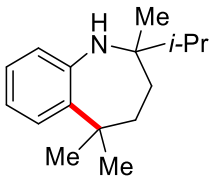
Prepared according to general procedure (D) (but for 35 h.) using **1p** to provide the title compound **2p** as a colorless oil (56.1 mg, 0.24 mmol, 81%). IR (neat, cm^{-1}) 2956, 2929, 2871, 1599, 1581, 1470, 1442, 1376, 1358, 1293, 1237, 1170, 1130, 1053, 949, 919, 850, 749, 700, 673, 505. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 7.6 Hz, 1H), 7.02 (t, *J* = 7.0 Hz, 1H), 6.90 (t, *J* = 7.3 Hz, 1H), 6.62 (d, *J* = 7.5 Hz, 1H), 3.07 (s, 1H), 1.85 – 1.60 (m, 4H), 1.50 – 1.20 (m, 10H), 1.06 (s, 3H), 0.95 – 0.80 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.8, 140.0, 126.6, 126.4, 123.1, 121.3, 55.0, 44.0, 38.2, 36.2, 36.1, 29.0, 27.0, 17.3, 14.9. HRMS (ESI) calcd. for $C_{16}H_{26}N$ $[M+H]^+$ *m/z* 232.2065, found 232.2074.

2-butyl-2,5,5-trimethyl-2,3,4,5-tetrahydro-1*H*-benzo[*b*]azepine (2q)



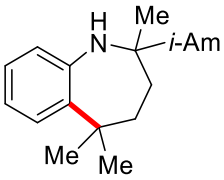
Prepared according to general procedure (D) using **1q** to provide the title compound **2q** as a colorless oil (46.3 mg, 0.19 mmol, 63%). IR (neat, cm^{-1}) 2955, 2928, 2859, 1599, 1581, 1469, 1442, 1375, 1358, 1294, 1268, 1236, 1169, 1130, 1088, 1053, 928, 851, 749, 699, 673, 505. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 7.7 Hz, 1H), 7.00 (t, *J* = 7.4 Hz, 1H), 6.88 (t, *J* = 7.5 Hz, 1H), 6.61 (d, *J* = 7.6 Hz, 1H), 2.94 (s, 1H), 1.87 – 1.69 (m, 2H), 1.69 – 1.59 (m, 2H), 1.41 – 1.21 (m, 12H), 1.04 (s, 3H), 0.88 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.8, 140.0, 126.6, 126.4, 123.2, 121.3, 54.9, 38.2, 36.2, 36.2, 29.3, 26.3, 25.9, 23.5, 14.3. HRMS (ESI) calcd. for $C_{17}H_{28}N$ $[M+H]^+$ *m/z* 246.2222, found 246.2224.

2-isopropyl-2,5,5-trimethyl-2,3,4,5-tetrahydro-1*H*-benzo[*b*]azepine (2r)



Prepared according to general procedure (D) (but with 140 °C for 35 h.) using **1r** to provide the title compound **2r** as a colorless oil (46.4 mg, 0.20 mmol, 67%). IR (neat, cm^{-1}) 2958, 1598, 1580, 1469, 1442, 1388, 1371, 1358, 1294, 1262, 1238, 1130, 1102, 1090, 1053, 949, 923, 852, 745, 690, 661, 601, 550, 531, 508. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.02 (td, *J* = 7.5, 1.3 Hz, 1H), 6.92 – 6.85 (m, 1H), 6.66 – 6.59 (m, 1H), 3.26 (s, 1H), 1.90 – 1.79 (m, 1H), 1.78 – 1.58 (m, 4H), 1.39 (s, 3H), 1.34 (s, 3H), 0.99 (s, 3H), 0.89 (d, *J* = 6.5 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.5, 139.9, 126.7, 126.4, 123.2, 121.1, 57.5, 38.4, 35.8, 33.6, 29.9, 22.6, 17.8, 16.9. HRMS (ESI) calcd. for $C_{16}H_{26}N$ $[M+H]^+$ *m/z* 232.2065, found 232.2070.

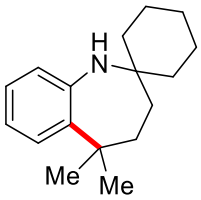
2-isopentyl-2,5,5-trimethyl-2,3,4,5-tetrahydro-1*H*-benzo[*b*]azepine (2s)



Prepared according to general procedure (D) (but for 35 h.) using **1s** to provide the title compound **2s** as a colorless oil (59.8 mg, 0.23 mmol, 77%). IR (neat, cm^{-1}) 2953, 2928, 2868, 1599, 1581, 1469, 1442, 1384, 1294, 1270, 1235, 1169, 1132, 1089, 1053, 948, 927, 851, 748, 699, 673, 504. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.00 (td, *J* = 7.5, 1.4 Hz, 1H), 6.89 (td, *J* = 7.7, 1.2 Hz, 1H), 6.62 (dd, *J* = 7.6, 1.1 Hz, 1H), 3.08 (s, 1H), 1.88 – 1.70 (m, 2H), 1.70 – 1.61 (m, 2H), 1.47 – 1.31 (m, 9H), 1.27 – 1.15 (m, 3H), 1.04 (s, 3H), 0.91

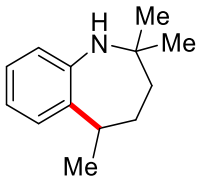
– 0.79 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.7, 140.0, 126.6, 126.4, 123.2, 121.3, 54.9, 38.2, 36.3, 36.2, 33.0, 29.3, 28.7, 26.7, 22.9, 22.8. HRMS (ESI) calcd. for $C_{18}H_{30}N$ $[M+H]^+$ *m/z* 260.2378, found 260.2381.

5,5-dimethyl-1,3,4,5-tetrahydrospiro[benzo[*b*]azepine-2,1'-cyclohexane] (2t)



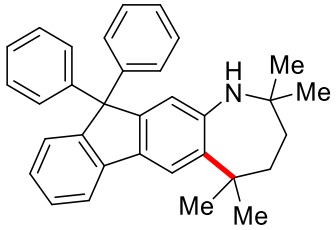
Prepared according to general procedure (D) (but for 35 h.) using **1t** to provide the title compound **2t** as a colorless oil (60.5 mg, 0.25 mmol, 83%). IR (neat, cm^{-1}) 2923, 2850, 1598, 1581, 1470, 1460, 1444, 1384, 1358, 1296, 1286, 1236, 1171, 1145, 1050, 992, 847, 748, 720, 687, 666, 506. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.24 (m, 1H), 7.02 (td, *J* = 7.5, 1.4 Hz, 1H), 6.89 (td, *J* = 7.7, 1.2 Hz, 1H), 6.73 – 6.67 (m, 1H), 3.45 (s, 1H), 1.77 – 1.69 (m, 2H), 1.69 – 1.61 (m, 2H), 1.61 – 1.41 (m, 8H), 1.38 – 1.28 (m, 8H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.1, 140.2, 126.6, 126.3, 123.2, 121.3, 53.6, 38.2, 37.4, 36.9, 35.6, 29.9, 26.1, 22.1. HRMS (ESI) calcd. for $C_{17}H_{26}N$ $[M+H]^+$ *m/z* 244.2065, found 244.2065.

2,2,5-trimethyl-2,3,4,5-tetrahydro-1*H*-benzo[*b*]azepine (2u)



Prepared according to general procedure (D) (but with DCE/Cy-H=1/1 as solvent.) using **1u** to provide the title compound **2u** as a colorless oil (22.7 mg, 0.12 mmol, 40%). IR (neat, cm^{-1}) 2959, 2922, 2852, 1462, 1377, 1259, 1086, 1015, 794, 701. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (d, *J* = 7.4 Hz, 1H), 7.01 (t, *J* = 7.2 Hz, 1H), 6.90 (t, *J* = 7.3 Hz, 1H), 6.65 (d, *J* = 7.5 Hz, 1H), 3.04 – 2.90 (m, 1H), 2.59 (s, 1H), 1.86 – 1.67 (m, 2H), 1.62 – 1.40 (m, 2H), 1.33 (d, *J* = 7.1 Hz, 3H), 1.18 (s, 3H), 1.08 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.1, 138.0, 127.2, 126.3, 121.8, 121.6, 52.6, 39.6, 37.1, 30.2, 30.0, 29.7, 19.4. HRMS (ESI) calcd. for $C_{13}H_{20}N$ $[M+H]^+$ *m/z* 190.1596, found 190.1600.

2,2,5,5-tetramethyl-11,11-diphenyl-1,2,3,4,5,11-hexahydrofluoreno[2,3-*b*]azepine (2ab)



Prepared according to general procedure (D) using **1ab** to provide the title compound **2ab** as a white solid (113.0 mg, 0.26 mmol, 85%). m.p.: 175 – 177 °C. IR (neat, cm^{-1}) 3415, 2957, 2861, 1611, 1514, 1490, 1447, 1413, 1383, 1352, 1322, 1291, 1268, 1234, 1217, 1188, 1161, 1117,

1099, 1079, 1030, 851, 813, 781, 757, 743, 726, 697, 635, 620, 599, 515.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.6 Hz, 2H), 7.33 (d, *J* = 7.5 Hz, 1H), 7.25 (t, *J* = 7.4 Hz, 1H), 7.22 – 7.09 (m, 11H), 6.65 (s, 1H), 3.04 (s, 1H), 1.83 – 1.55 (m, 2H), 1.44 (s, 6H), 1.06 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.8, 149.5, 146.5, 146.4, 141.0, 139.8, 133.7, 128.3, 128.2, 127.4, 126.5, 126.3, 126.1, 120.9, 119.1, 118.1, 65.1, 52.8, 38.2, 36.7, 29.2.
^{1}H NMR (400 MHz, DMSO-d_6) δ 7.77 (d, *J* = 7.5 Hz, 1H), 7.67 (s, 1H), 7.31 (t, *J* = 7.9 Hz, 2H), 7.28 – 7.14 (m, 7H), 7.10 (d, *J* = 7.0 Hz, 4H), 7.00 (s, 1H), 4.43 (s, 1H), 1.79 – 1.51 (m, 4H), 1.38 (s, 6H), 1.04 (s, 6H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 150.0, 148.6, 147.3, 146.1, 140.6, 138.9, 132.1, 128.1, 127.7, 127.4, 126.4, 125.9, 125.8, 120.5, 119.2, 117.8, 64.3, 52.2, 37.8, 36.1, 28.7.

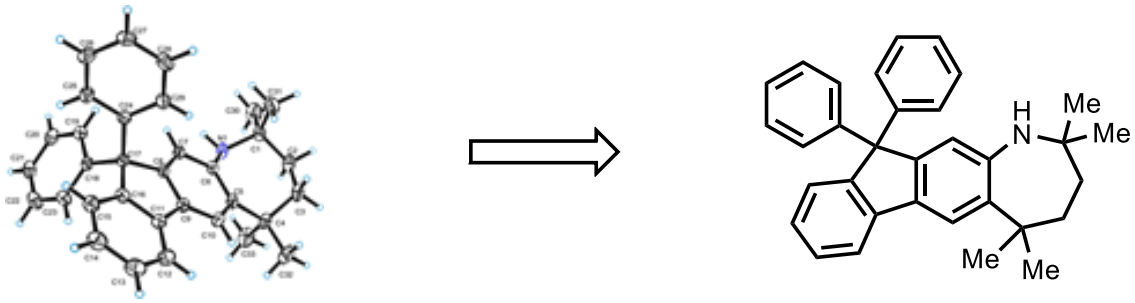
To verify the definite configuration of the products, the NMR analysis at 353 K and X-ray crystallographic analysis of **2z** were conducted as a pilot example to other products **2**.
^{1}H NMR (400 MHz, DMSO-d_6, 353 K) δ 7.75 (dd, *J* = 7.3, 1.1 Hz, 1H), 7.68 (s, 1H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.27 – 7.16 (m, 7H), 7.16 – 7.12 (m, 4H), 6.98 (s, 1H), 4.17 (s, 1H), 1.68 (s, 4H), 1.42 (s, 6H), 1.07 (s, 6H); ^{13}C NMR (101 MHz, DMSO-d_6, 353 K) δ 149.8, 148.5, 146.5, 145.6, 140.3, 138.8, 132.0, 127.5, 127.3, 126.9, 125.8, 125.4, 120.3, 118.6, 117.3, 64.1, 52.0, 37.5, 35.9, 28.4, 28.1.
HRMS (ESI) calcd. for $C_{33}H_{34}N$ $[M+H]^+$ *m/z* 444.2691, found 444.2703.

X-ray crystallographic structure of 2z.
The configuration of **2z** was confirmed by X-ray crystallographic analysis.

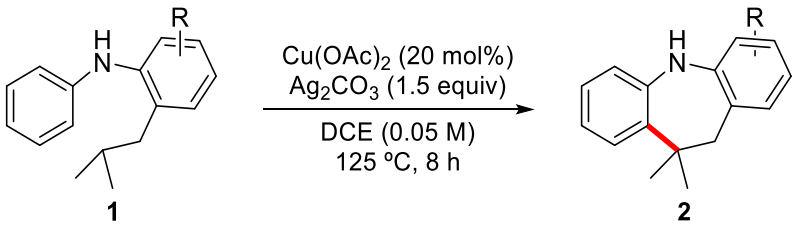
Table 1 Crystal data and structure refinement for wr-7.

Identification code	wr-7
Empirical formula	$C_{33}H_{33}N$
Formula weight	443.60
Temperature/K	291(2)
Crystal system	triclinic
Space group	P-1
a/Å	8.9337(2)
b/Å	10.9430(4)
c/Å	13.0698(4)
α/°	92.791(3)
β/°	97.221(2)
γ/°	94.987(2)
Volume/Å^3	1260.49(7)
Z	2
ρ_{calc}g/cm^3	1.169
μ/mm^{-1}	0.502
F(000)	476.0
Crystal size/mm^3	0.240 × 0.220 × 0.210
Radiation	CuKα (λ = 1.54184)

2Θ range for data collection/°	6.83 to 142.468
Index ranges	$-10 \leq h \leq 6, -12 \leq k \leq 13, -15 \leq l \leq 15$
Reflections collected	8360
Independent reflections	4740 [R_{int} = 0.0195, R_{sigma} = 0.0263]
Data/restraints/parameters	4740/1/316
Goodness-of-fit on F^2	1.052
Final R indexes [I>=2σ (I)]	R_1 = 0.0473, wR_2 = 0.1308
Final R indexes [all data]	R_1 = 0.0529, wR_2 = 0.1369
Largest diff. peak/hole / e $Å^{-3}$	0.51/-0.19



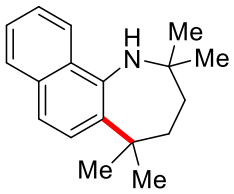
Single crystal of **2z** [$C_{33}H_{33}N$] was obtained from acetone. CCDC 1562122 contains the supplementary crystallographic data which can be obtained free of charge from The Cambrige Crystallographic Data Centere via www.ccdc.cam.ac.uk/data_request/cif.



1 **2**

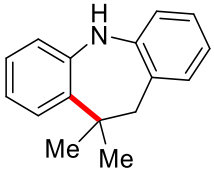
Genaral procedure (E) for the novel and facile synthesis of 1-benzazepines via copper-catalyzed oxidative C(sp^3)-H/C(sp^2)-H cross-coupling. To an oven-dried 35 mL screw-cap sealed tube equipped with a magnetic stir bar was added Cu(OAc)2 (20 mol%), Ag2CO3 (1.5 equiv), substrate **1** (0.3 mmol, 1.0 equiv) and 1,2-dichloroethane (6.0 mL) at air atmosphere. The vessel was then sealed with a Teflon screw-cap, stirred vigorously at rt for 5 min, and placed into a preheated oil bath at 125 °C for 8 h. After completion, the reaction mixture was allowed to cool to room temperature, and was directly filtered through a short pad of silica gel washed with EtOAc. The filtrate was concentrated under vacuum and purified by column chromatography on silica gel to obtain the corresponding product **2**.

2,2,5,5-tetramethyl-2,3,4,5-tetrahydro-1*H*-naphtho[1,2-*b*]azepine (2f)



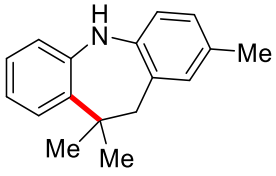
Prepared according to general procedure (E) (but with 20 h) using **1f** to provide the title compound **2f** as a yellow oil (45.7 mg, 0.21 mmol, 69%). IR (neat, cm^{-1}) 3408, 2956, 2923, 1566, 1513, 1479, 1468, 1444, 1378, 1361, 1438, 1294, 1270, 1233, 1208, 1170, 1147, 1135, 1081, 1031, 935, 913, 891, 851, 807, 785, 736, 683, 658, 635, 597, 582. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.5 Hz, 1H), 7.79 (d, *J* = 7.9 Hz, 1H), 7.54 (d, *J* = 8.7 Hz, 1H), 7.45 (d, *J* = 8.8 Hz, 1H), 7.40 (t, *J* = 7.2 Hz, 1H), 3.99 (s, 1H), 1.71 – 1.71 (m, 4H), 1.48 (s, 6H), 1.22 (s, 6H).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.4, 136.1, 133.2, 129.0, 128.5, 125.8, 125.4, 124.8, 121.4, 121.2, 53.1, 38.6, 38.4, 36.7, 29.2. HRMS (ESI) calcd. for $C_{14}H_{21}NF$ $[M+H]^+$ *m/z* 254.1909, found 254.1902.

10,10-dimethyl-10,11-dihydro-5*H*-dibenzo[*b*,*f*]azepine (2v)



Prepared according to general procedure (E) using **1v** to provide the title compound **2v** as a colorless oil (46.8 mg, 0.21 mmol, 70%). IR (neat, cm^{-1}) 3389, 2957, 2924, 1612, 1590, 1526, 1481, 1444, 1385, 1363, 1338, 1273, 1247, 1213, 1155, 1120, 1086, 1053, 968, 933, 898, 846, 739, 689, 660, 622, 607, 569, 524, 495, 449. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.15 – 7.03 (m, 3H), 6.88 – 6.79 (m, 2H), 6.79 – 6.71 (m, 2H), 5.93 (s, 1H), 2.98 (s, 2H), 1.34 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2, 141.8, 135.3, 131.4, 128.4, 128.0, 127.0, 126.8, 120.3, 119.6, 119.3, 117.3, 47.9, 37.9, 31.5. HRMS (ESI) calcd. for $C_{16}H_{18}N$ $[M+H]^+$ *m/z* 224.1439, found 224.1445.

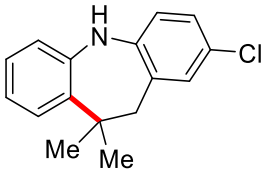
2,10,10-trimethyl-10,11-dihydro-5*H*-dibenzo[*b*,*f*]azepine (2w)



Prepared according to general procedure (E) (but for 6 h.) using **1w** to provide the title compound **2w** as a colorless oil (51.2 mg, 0.22 mmol, 72%). IR (neat, cm^{-1}) 3379, 2958, 2923, 1614, 1594, 1509, 1487, 1435, 1383, 1362, 1337, 1277, 1258, 1209, 1166, 1156, 1132, 1115, 1087, 1054, 979, 933, 907, 887, 813, 748, 653, 630, 564, 524, 504, 471, 451. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.09 – 7.02 (m, 1H), 6.91 (d, *J* = 7.5 Hz, 2H), 6.84 – 6.78 (m, 1H), 6.75 – 6.70 (m, 1H), 6.67 (d, *J* = 7.7 Hz, 1H), 5.83 (s, 1H), 2.95 (s, 2H), 2.29 (s, 3H), 1.34 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.1, 140.9, 135.1, 131.9, 129.6, 128.5, 128.1, 127.5, 126.8, 119.3, 119.2, 117.3, 47.7, 37.8, 31.6, 20.7. HRMS (ESI) calcd. for

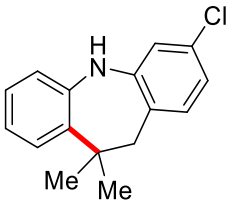
$C_{17}H_{20}N$ $[M+H]^+$ *m/z* 238.1596, found 238.1599.

2-chloro-10,10-dimethyl-10,11-dihydro-5*H*-dibenzo[*b*,*f*]azepine (2x)



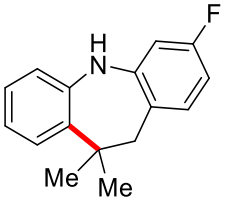
Prepared according to general procedure (E) using **1x** to provide the title compound **2x** as a colorless oil (59.4 mg, 0.23 mmol, 77%). IR (neat, cm^{-1}) 3381, 2957, 2923, 1612, 1593, 1508, 1486, 1435, 1383, 1362, 1339, 1276, 1258, 1208, 1165, 1131, 1115, 1087, 1053, 886, 809, 748, 693, 629, 563, 523, 503, 481, 472, 451. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.11 – 7.02 (m, 3H), 6.87 – 6.81 (m, 1H), 6.75 – 6.71 (m, 1H), 6.71 – 6.65 (m, 1H), 5.91 (s, 1H), 2.93 (s, 2H), 1.33 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.8, 141.3, 135.2, 130.8, 129.6, 128.3, 126.9, 126.8, 124.9, 119.9, 119.4, 118.5, 47.6, 37.8, 31.4. HRMS (ESI) calcd. for $C_{16}H_{17}NCl$ $[M+H]^+$ *m/z* 258.1050, found 258.1051.

3-chloro-10,10-dimethyl-10,11-dihydro-5*H*-dibenzo[*b*,*f*]azepine (2y)



Prepared according to general procedure (E) (but for 6 h.) using **1y** to provide the title compound **2y** as a colorless oil (54.0 mg, 0.21 mmol, 70%). IR (neat, cm^{-1}) 3390, 2958, 2924, 1607, 1581, 1527, 1481, 1397, 1384, 1364, 1342, 1331, 1263, 1197, 1086, 1052, 975, 935, 839, 790, 746, 696, 665, 609, 584, 497, 480, 457. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.9 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.98 (d, *J* = 7.9 Hz, 1H), 6.85 (t, *J* = 7.5 Hz, 1H), 6.79 (d, *J* = 7.9 Hz, 1H), 6.78 – 6.76 (m, 1H), 6.72 (d, *J* = 8.0 Hz, 1H), 5.94 (s, 1H), 2.92 (s, 2H), 1.32 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.0, 141.1, 135.5, 132.5, 132.2, 128.1, 127.0, 126.1, 120.1, 120.0, 119.5, 117.0, 47.5, 37.8, 31.1. HRMS (ESI) calcd. for $C_{16}H_{17}NCl$ $[M+H]^+$ *m/z* 258.1050, found 258.1051.

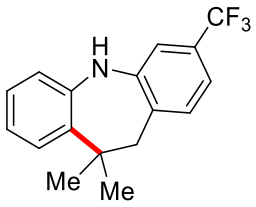
3-fluoro-10,10-dimethyl-10,11-dihydro-5*H*-dibenzo[*b*,*f*]azepine (2z)



Prepared according to general procedure (E) (but for 6 h.) using **1z** to provide the title compound **2z** as a colorless oil (59.3 mg, 0.25 mmol, 82%). IR (neat, cm^{-1}) 3390, 2957, 2926, 1615, 1598, 1582, 1505, 1482, 1385, 1364, 1344, 1275, 1252, 1221, 1151, 1116, 1104, 1087, 1052, 993, 935, 836, 803, 747, 694, 607. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (dd, *J* = 7.9, 1.2

Hz, 1H), 7.11 – 7.04 (m, 1H), 7.03 – 6.96 (m, 1H), 6.89 – 6.81 (m, 1H), 6.76 – 6.70 (m, 1H), 6.53 (td, *J* = 8.3, 2.5 Hz, 1H), 6.47 (dd, *J* = 10.3, 2.4 Hz, 1H), 5.94 (s, 1H), 2.92 (s, 2H), 1.32 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.0 (d, *J* = 242.4 Hz), 144.1 (d, *J* = 9.9 Hz), 141.2, 135.5, 132.5 (d, *J* = 9.5 Hz), 128.2, 126.9, 123.4, 123.4, 120.1, 119.4, 106.8 (d, *J* = 21.0 Hz), 103.9 (d, *J* = 24.2 Hz), 47.3, 37.8, 31.1. HRMS (ESI) calcd. for $C_{16}H_{17}NF$ $[M+H]^+$ *m/z* 242.1345, found 242.1348.

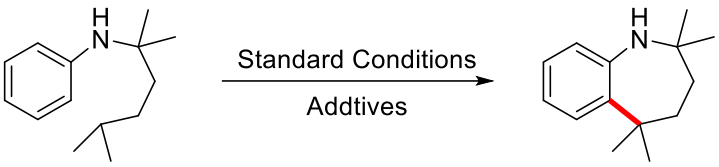
10,10-dimethyl-3-(trifluoromethyl)-10,11-dihydro-5*H*-dibenzo[*b,f*]azepine (2aa)



Prepared according to general procedure (E) (but for 6 h.) using **1aa** to provide the title compound **2aa** as a colorless oil (72.5 mg, 0.25 mmol, 83%). IR (neat, cm^{-1}) 3394, 2962, 1591, 1541, 1510, 1485, 1410, 1388, 1322, 1243, 1160, 1114, 1074, 1052, 976, 937, 866, 846, 805, 747, 686, 657. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.17 (d, *J* = 7.8 Hz, 1H), 7.13 – 7.07 (m, 1H), 7.06 (d, *J* = 8.0 Hz, 1H), 7.01 (s, 1H), 6.90 – 6.83 (m, 1H), 6.79 – 6.73 (m, 1H), 6.07 (s, 1H), 3.00 (s, 2H), 1.34 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2, 141.0, 135.4, 131.9, 131.2, 129.5 (q, *J* = 32.3 Hz), 128.2, 127.1, 124.3 (q, *J* = 273.0 Hz), 120.3, 119.5, 116.6 (q, *J* = 3.8 Hz), 114.0 (q, *J* = 3.7 Hz), 47.9, 37.8, 31.2. HRMS (ESI) calcd. for $C_{17}H_{17}NF_3$ $[M+H]^+$ *m/z* 292.1313, found 292.1317.

IV. Mechanism Details.

Table S8 | Effects of Radical Inhibitors



entry	Addtives	yield[a]
1	TEMPO (1.0 eq.)	0
2	TEMPO (0.5 eq.)	0
3	TEMPO (0.3 eq.)	trace
4	Galvinoxyl (1.0 eq.)	0
5	Galvinoxyl (0.5 eq.)	0
6	Galvinoxyl (0.3 eq.)	0
7	BHT (1.0 eq.)	0
8	BHT (0.5 eq.)	0
9	BHT (0.3 eq.)	trace

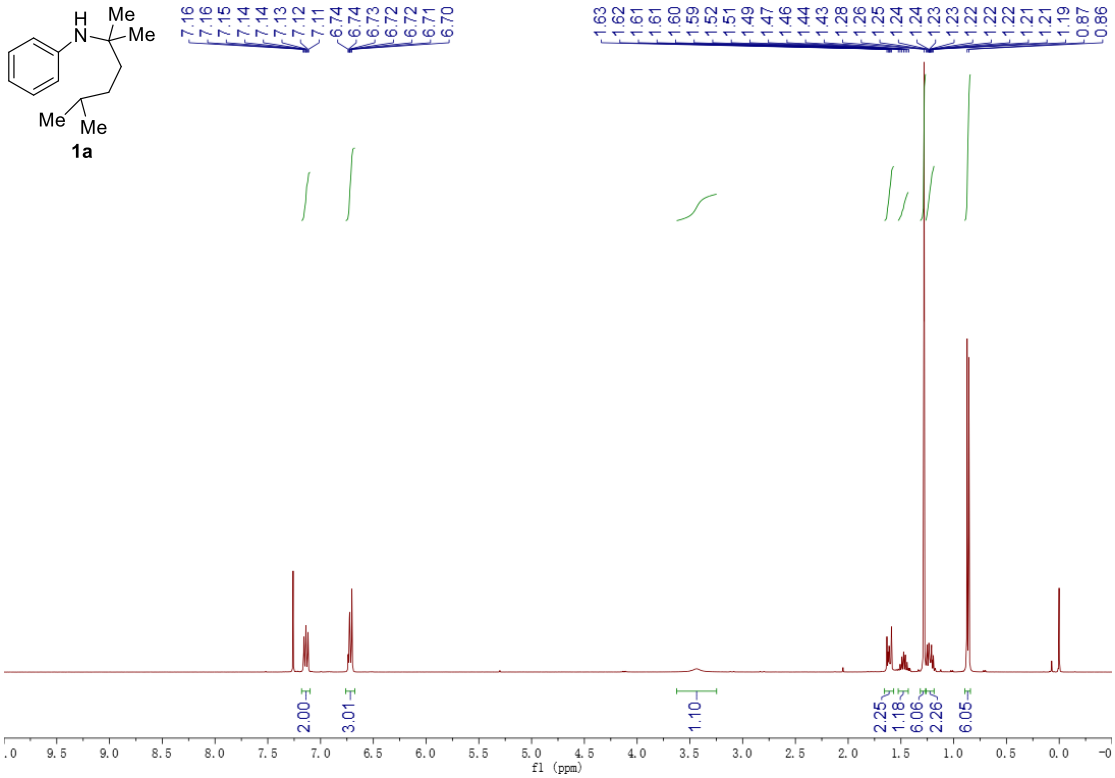
[a]Determined by TLC and isolating.

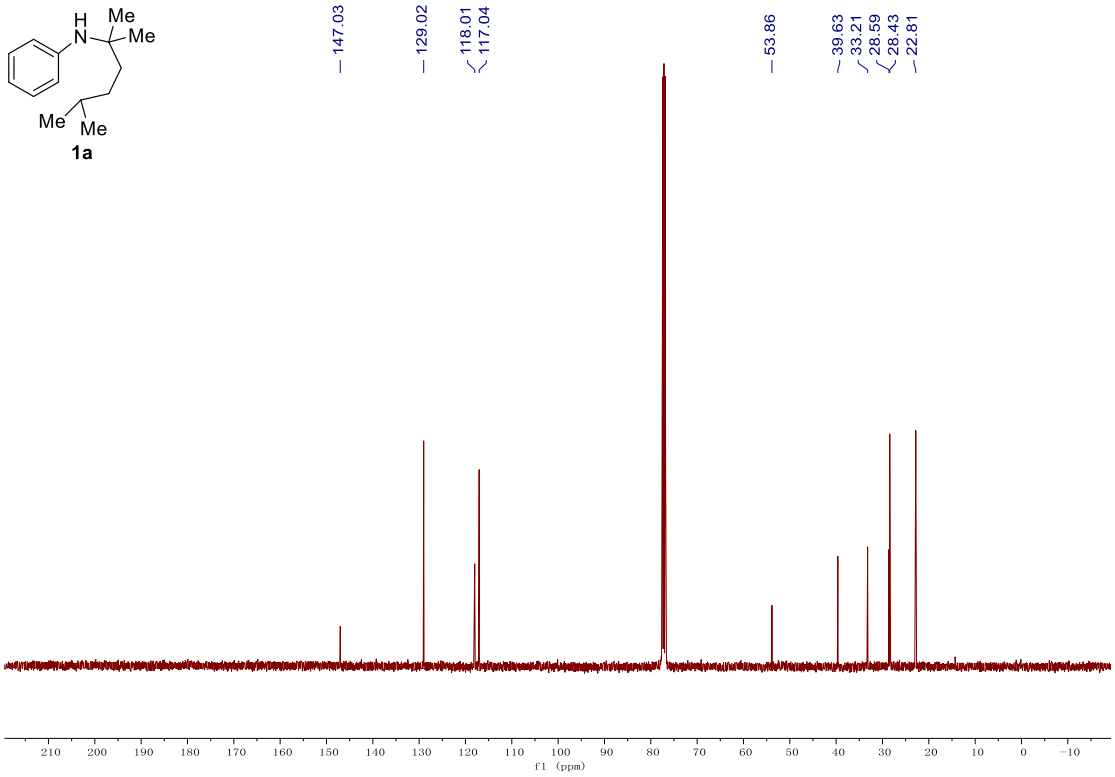
V. References.

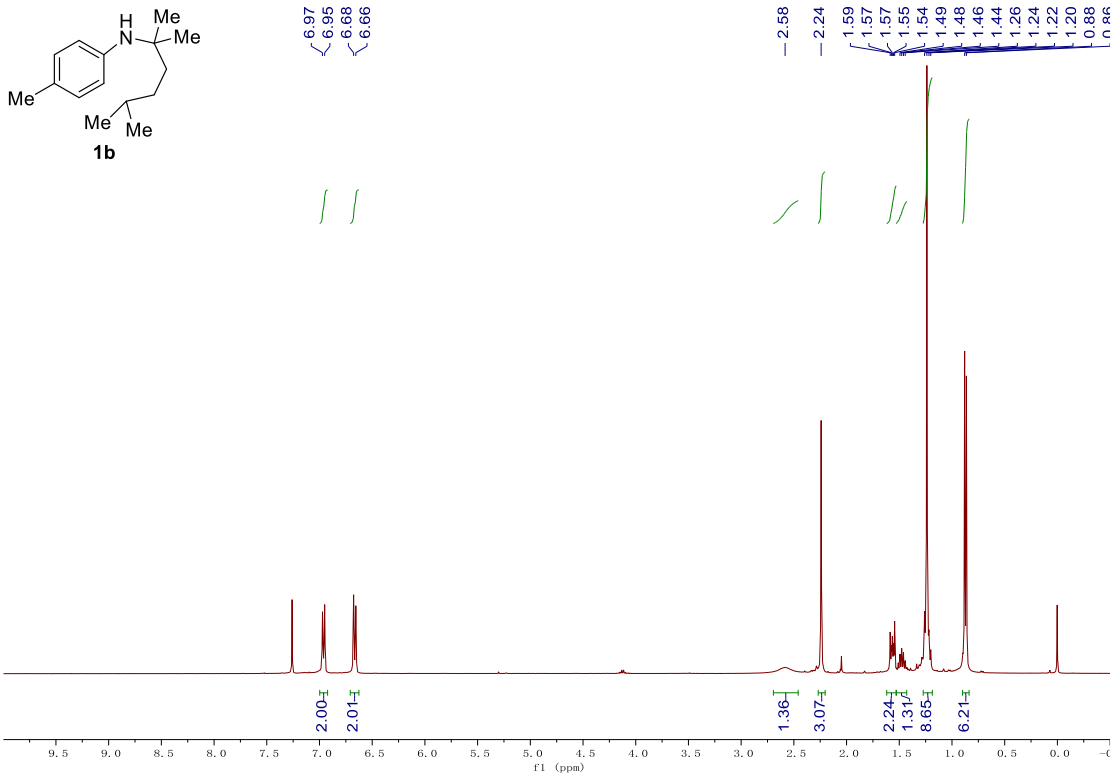
[1] Barros, M. T.; Dey, S. S.; Maycock, C. D.; Rodrigues, P. *Chem. Commun*., **2012**, *48*, 10901.

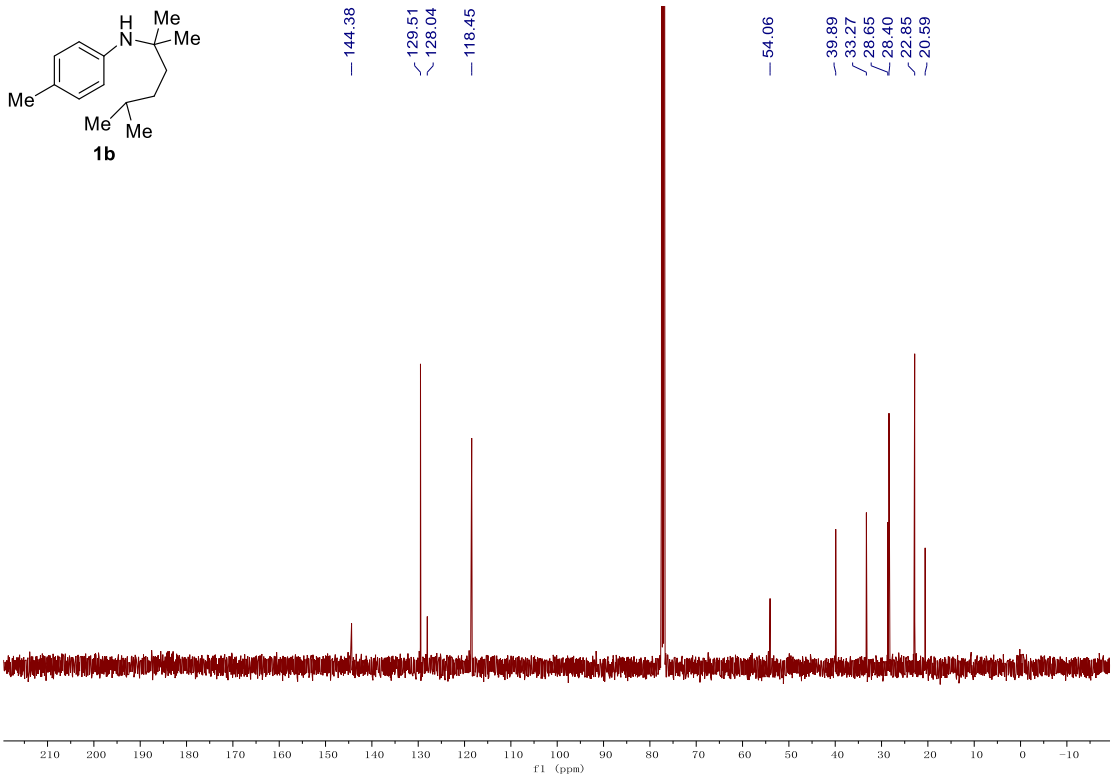
[2] Tewari, A.; Hein, M.; Zapf, A.; Beller, M. *Tetrahedron*, **2005**, *61*, 9705.

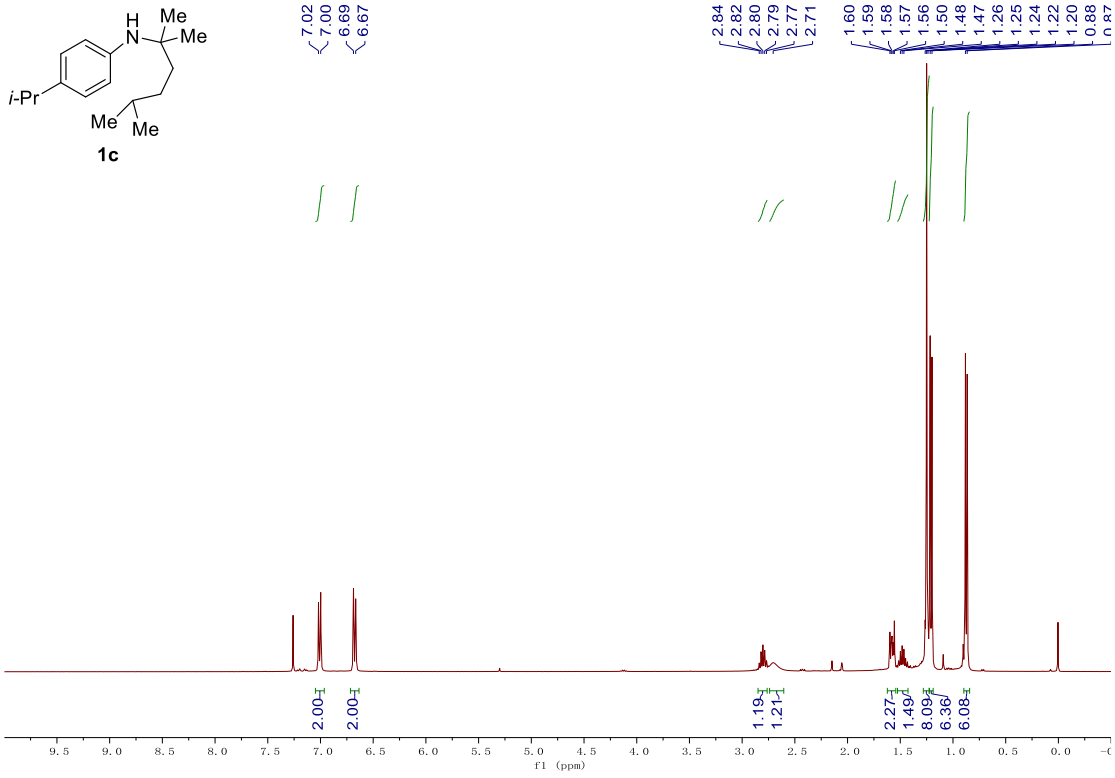
VI. Spectroscopic Data (NMR Spectrum).

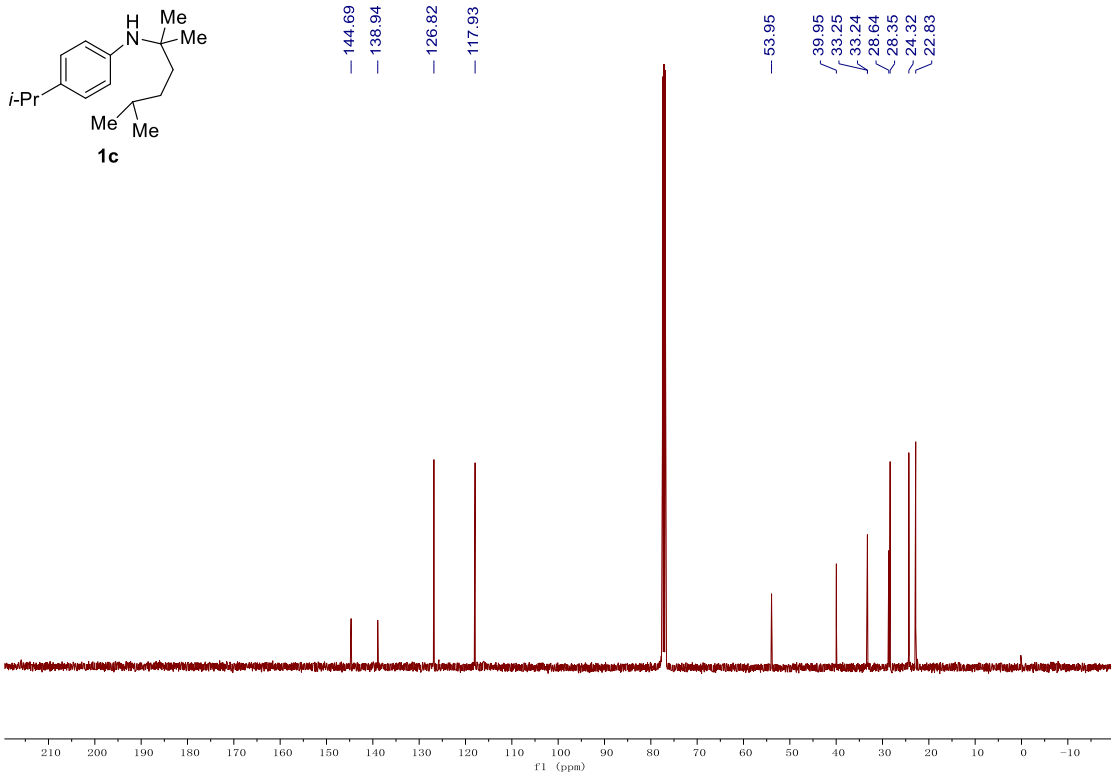


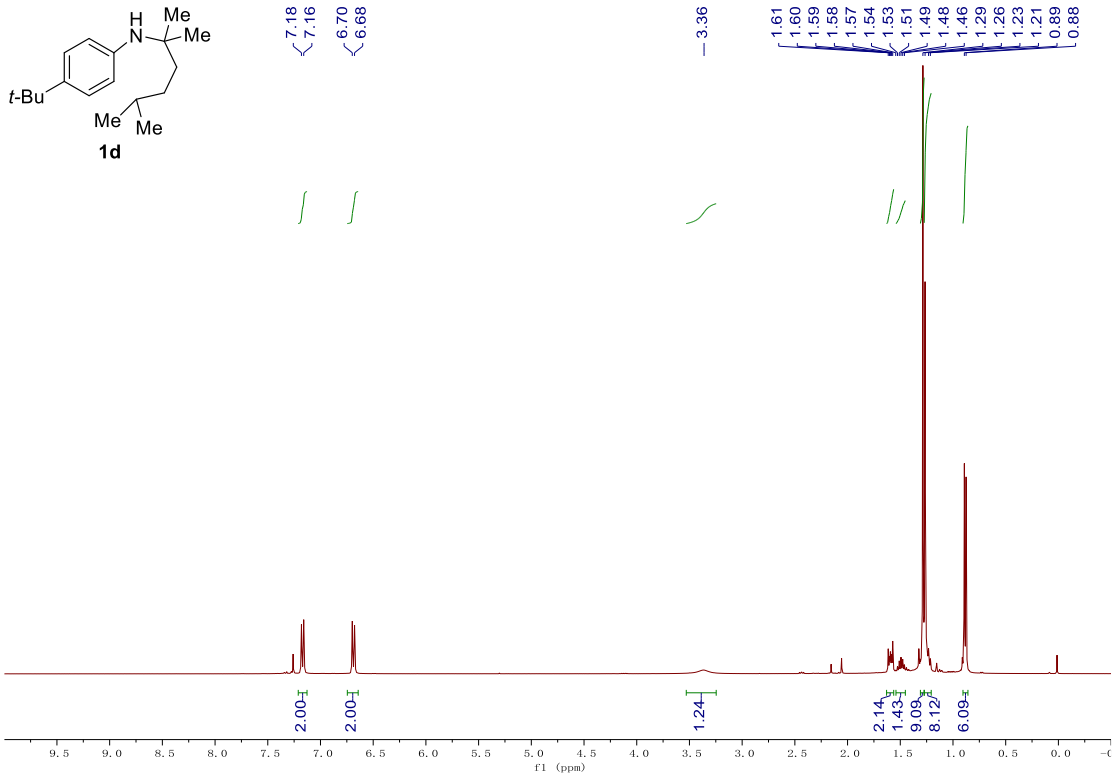


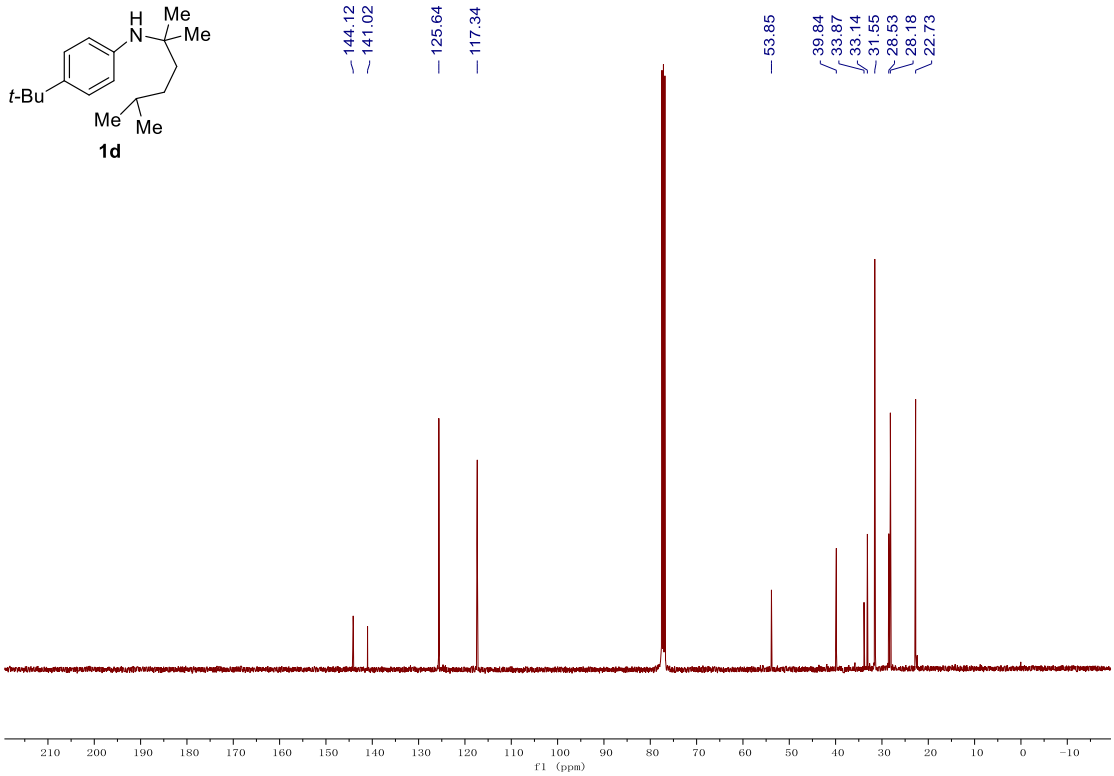

1b
6.97
6.95
6.68
6.66
2.58
2.24
1.59
1.57
1.57
1.55
1.54
1.49
1.48
1.46
1.44
1.26
1.24
1.22
1.20
0.88
2.00
2.01
1.36
3.07
2.24
1.31
8.65
6.21
f1 (ppm)

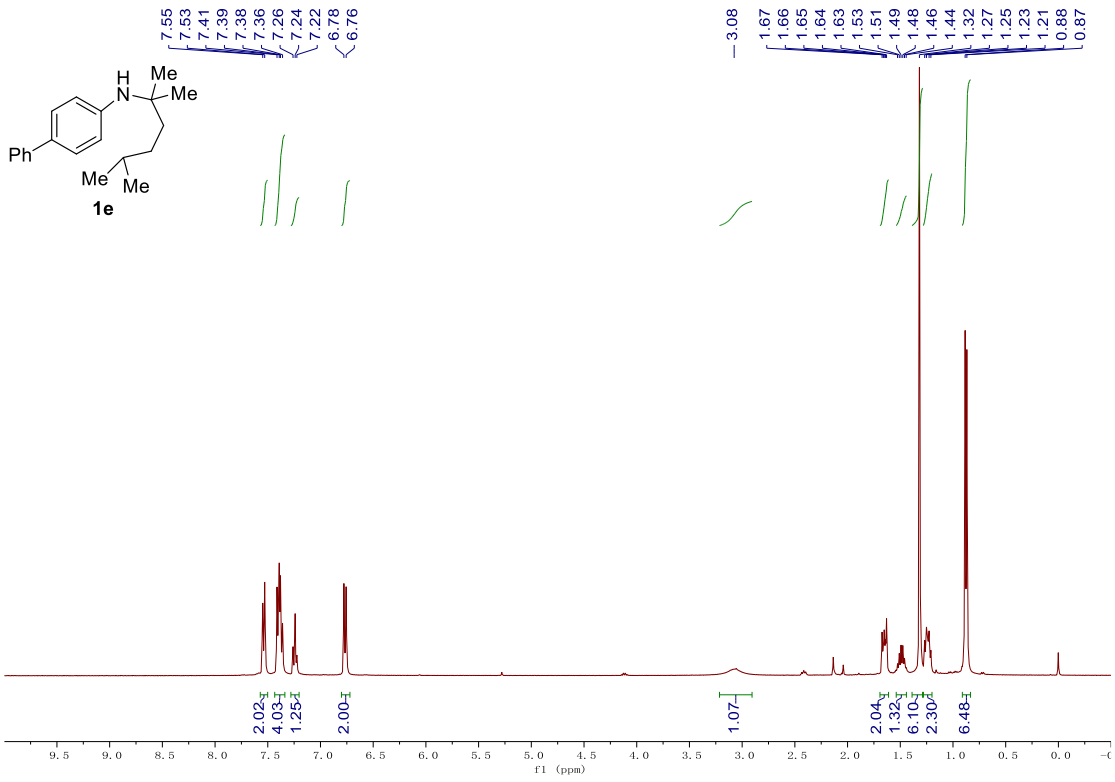

1b
144.38
129.51
128.04
118.45
54.06
39.89
33.27
28.65
28.40
22.85
20.59
f1 (ppm)

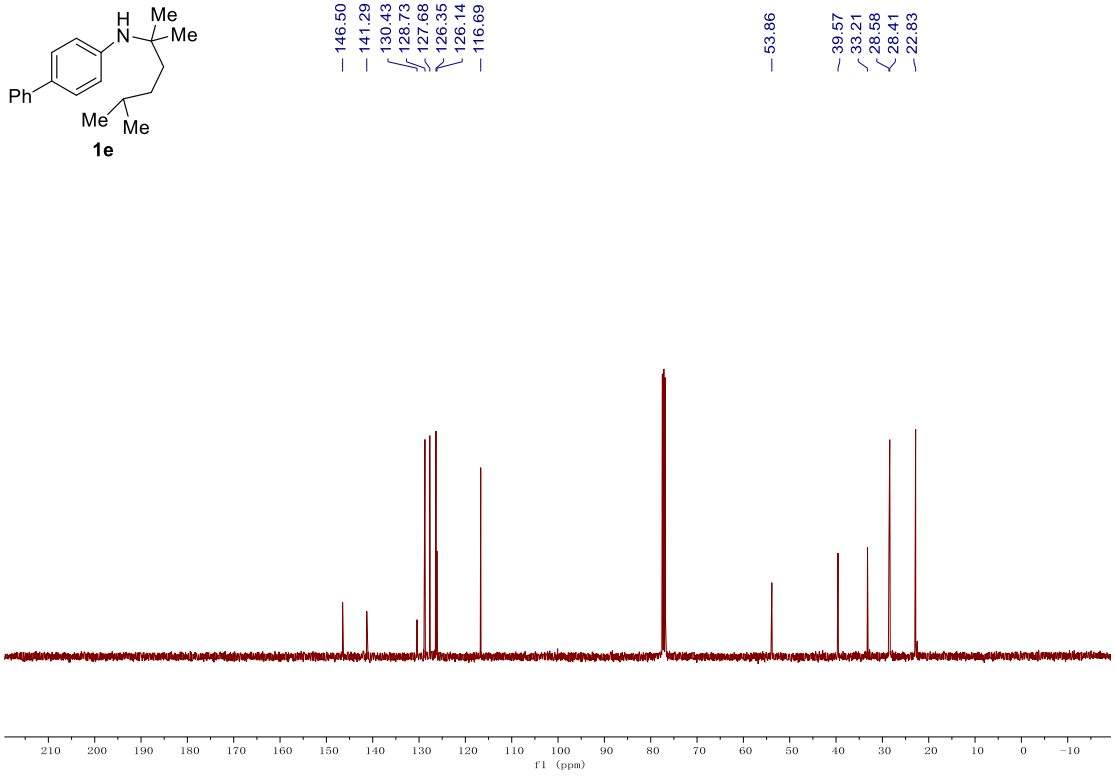

i-Pr
Me
Me
Me
Me
H
N
1c
7.02
7.00
6.69
6.67
2.84
2.82
2.80
2.79
2.77
2.71
1.60
1.59
1.58
1.57
1.56
1.50
1.48
1.47
1.26
1.25
1.24
1.22
1.20
0.88
2.00
2.00
1.19
1.21
2.27
1.49
8.09
6.36
6.08
f1 (ppm)

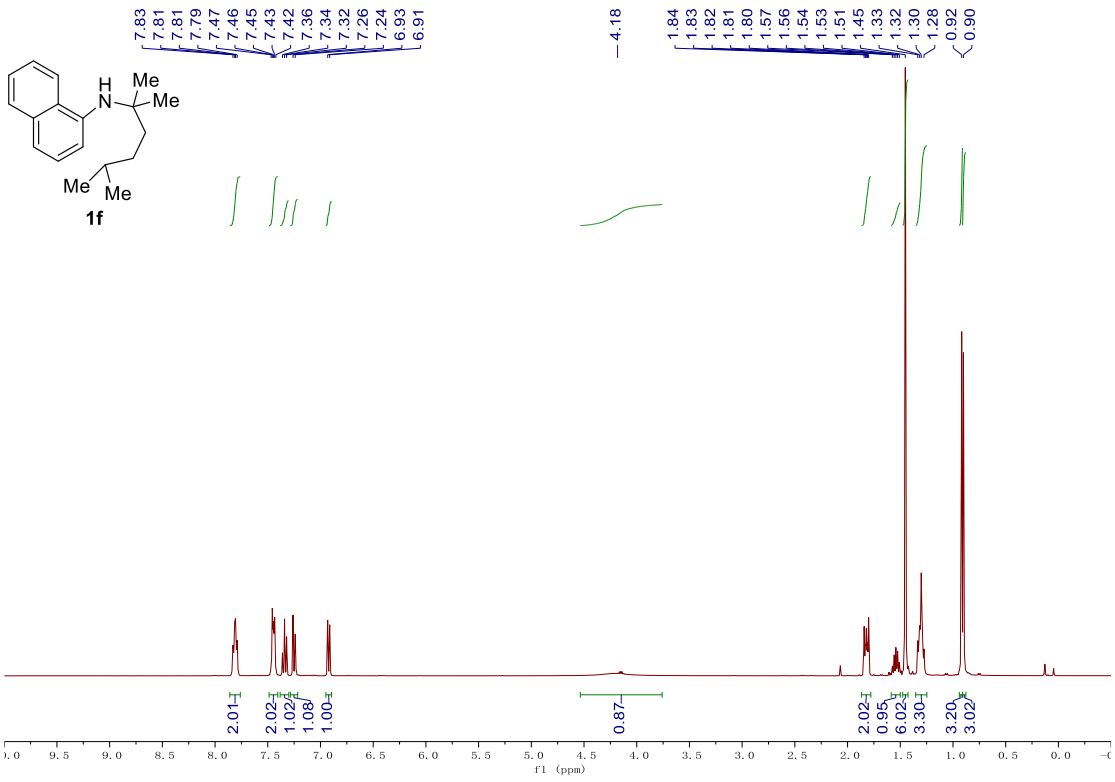

i-Pr
Me
Me
Me
Me
H
N
1c
144.69
138.94
126.82
117.93
53.95
39.95
33.25
33.24
28.64
28.35
24.32
22.83
f1 (ppm)

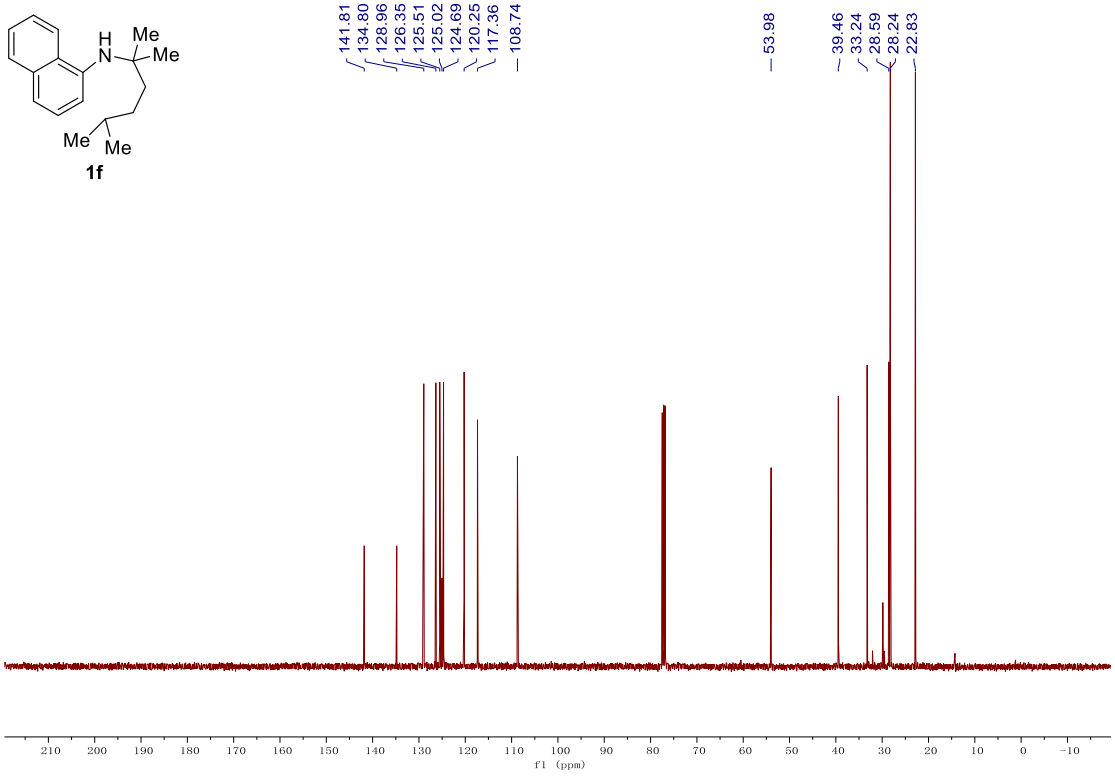

H
N
Me
Me
t-Bu
Me
Me
1d
7.18
7.16
6.70
6.68
3.36
1.61
1.60
1.59
1.58
1.57
1.54
1.53
1.51
1.49
1.48
1.46
1.29
1.26
1.23
1.21
0.89
0.88
2.00
2.00
1.24
2.14
1.43
9.09
8.12
6.09
f1 (ppm)

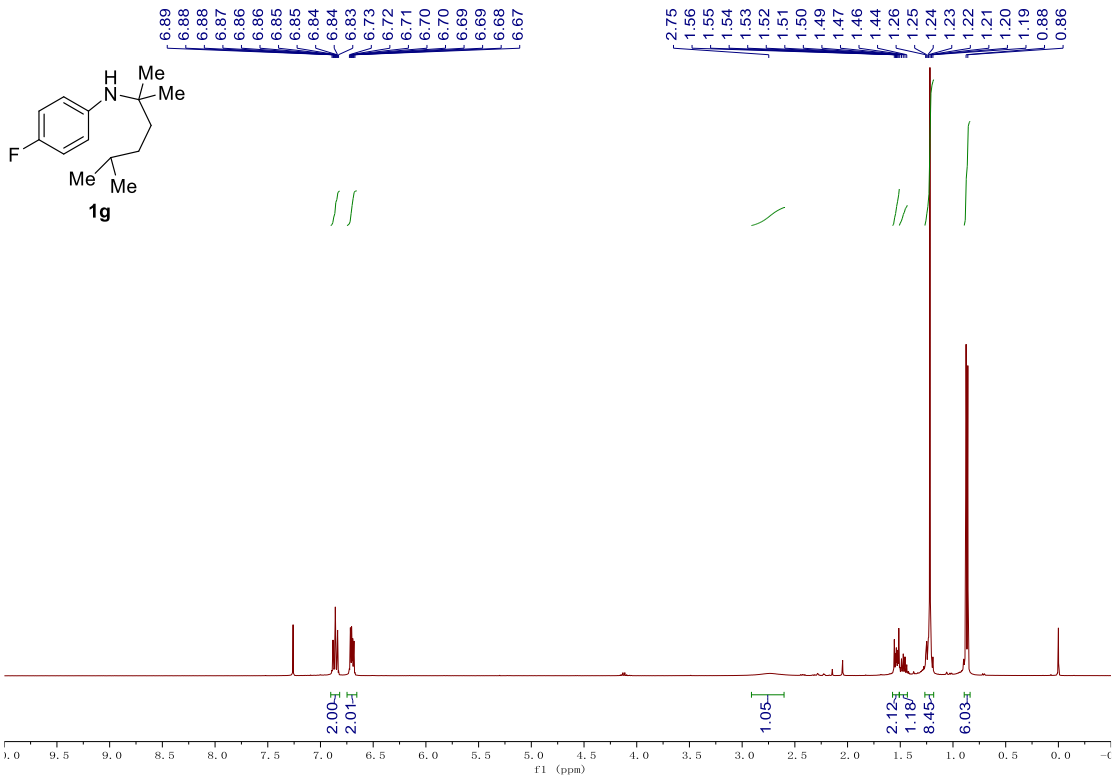

H
N
Me
Me
t-Bu
Me
Me
1d
144.12
141.02
125.64
117.34
53.85
39.84
33.87
33.14
31.55
28.53
28.18
22.73
f1 (ppm)

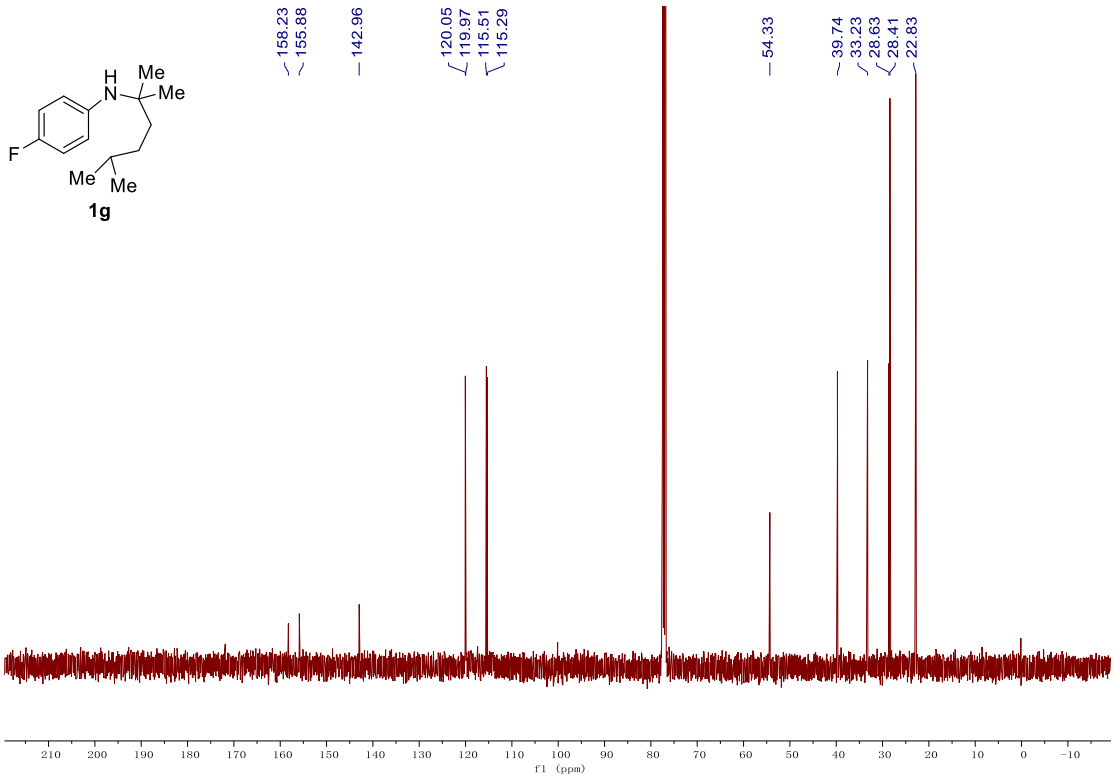

7.55
7.53
7.41
7.39
7.38
7.36
7.26
7.24
7.22
6.78
6.76
3.08
1.67
1.66
1.65
1.64
1.63
1.53
1.51
1.49
1.48
1.46
1.44
1.32
1.27
1.25
1.23
1.21
0.88
0.87
H
N
Me
Me
Ph
Me
Me
1e
2.02
4.03
1.25
2.00
1.07
2.04
1.32
6.10
2.30
6.48
f1 (ppm)

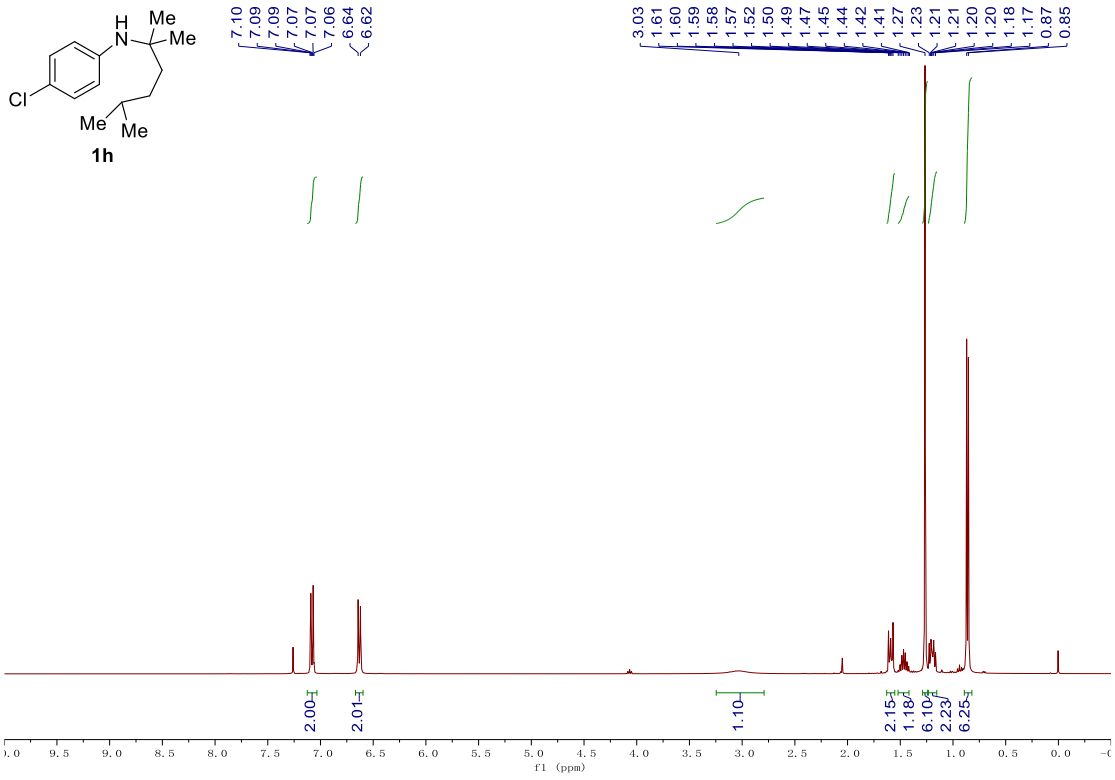

146.50
141.29
130.43
128.73
127.68
126.35
126.14
116.69
53.86
39.57
33.21
28.58
28.41
22.83
H
N
Me
Me
Ph
Me
Me
1e
f1 (ppm)

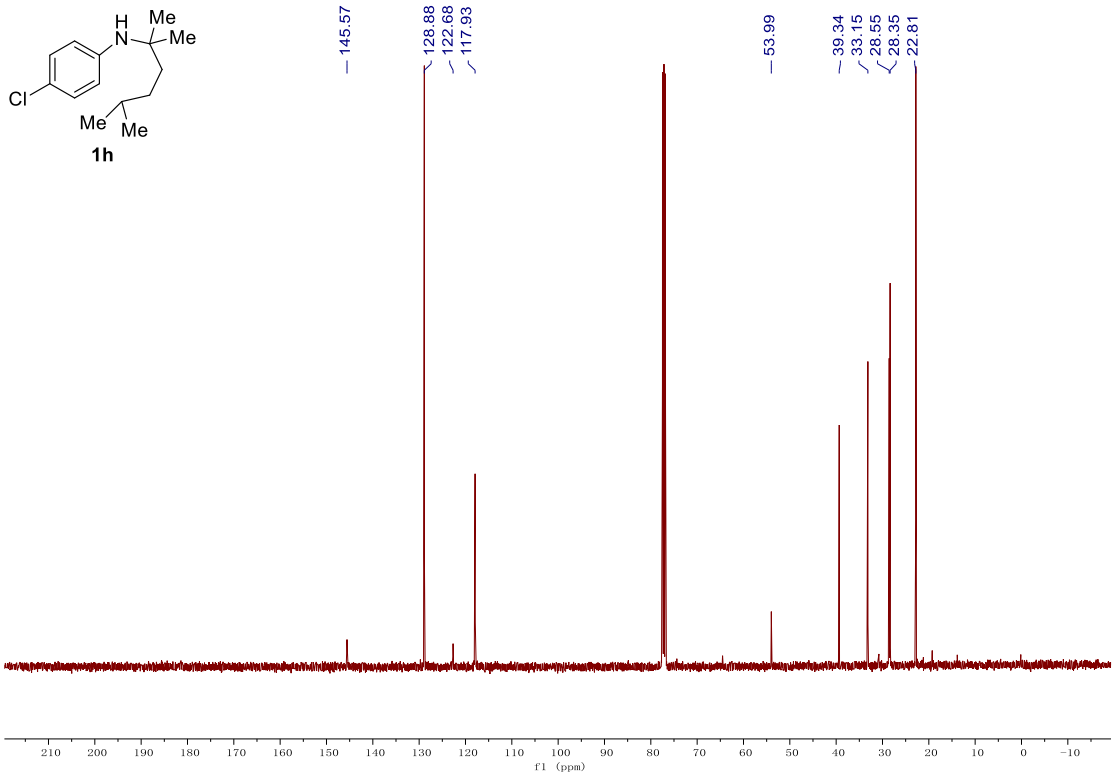

7.83
7.81
7.81
7.79
7.47
7.46
7.45
7.43
7.42
7.36
7.34
7.32
7.26
7.24
6.93
6.91
4.18
1.84
1.83
1.82
1.81
1.80
1.57
1.56
1.54
1.53
1.51
1.45
1.33
1.32
1.30
1.28
0.92
0.90
H
N
Me
Me
Me
Me
1f
2.01
2.02
1.02
1.08
1.00
0.87
2.02
0.95
6.02
3.30
3.20
3.02
f1 (ppm)

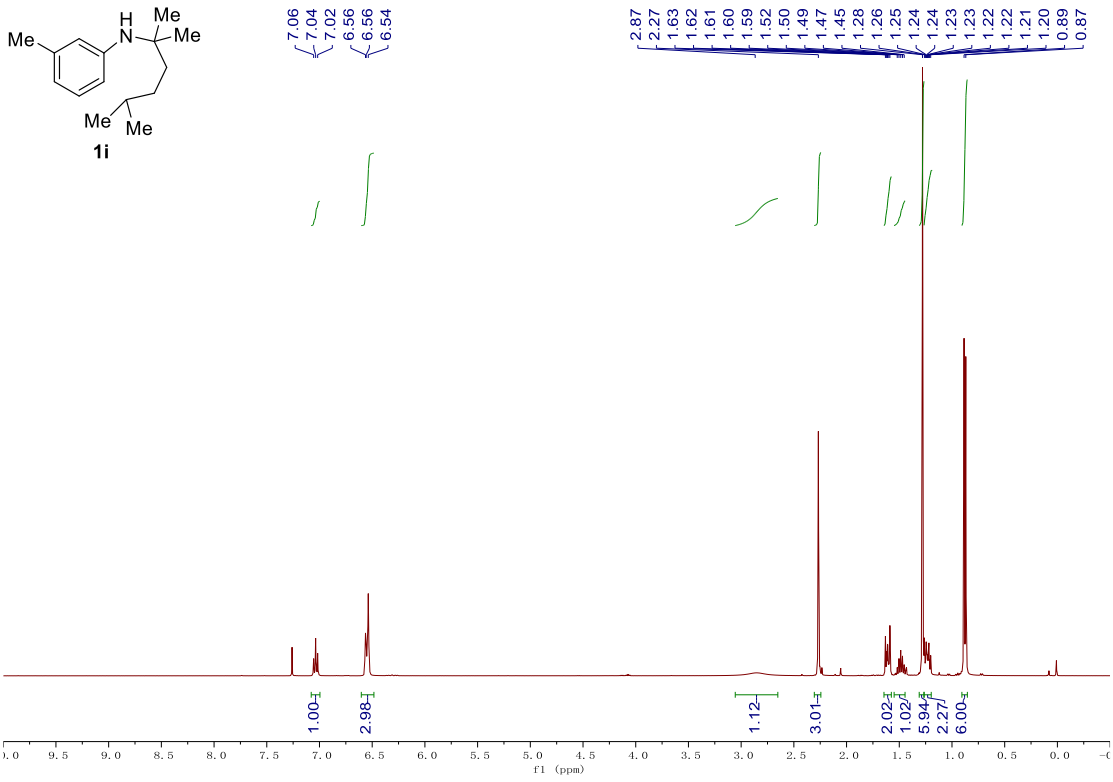

141.81
134.80
128.96
126.35
125.51
125.02
124.69
120.25
117.36
108.74
53.98
39.46
33.24
28.59
28.24
22.83
H
N
Me
Me
Me
Me
1f
f1 (ppm)

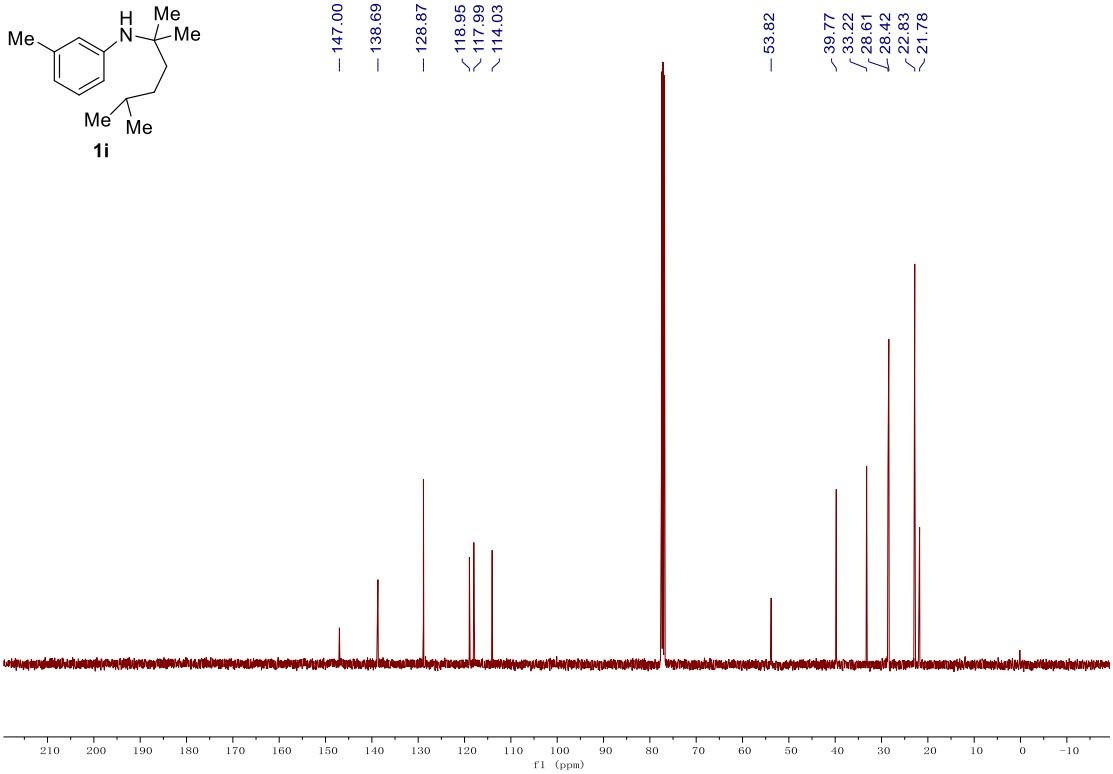

6.89 6.88 6.88 6.87 6.86 6.86 6.85 6.85 6.84 6.84 6.83 6.73 6.72 6.71 6.70 6.70 6.69 6.69 6.68 6.67
2.75 1.56 1.55 1.54 1.53 1.52 1.51 1.50 1.49 1.47 1.46 1.44 1.26 1.25 1.24 1.23 1.22 1.21 1.20 1.19 0.88 0.86
H N Me Me F Me Me
1g
2.00 2.01 1.05 2.12 1.18 8.45 6.03
f1 (ppm)

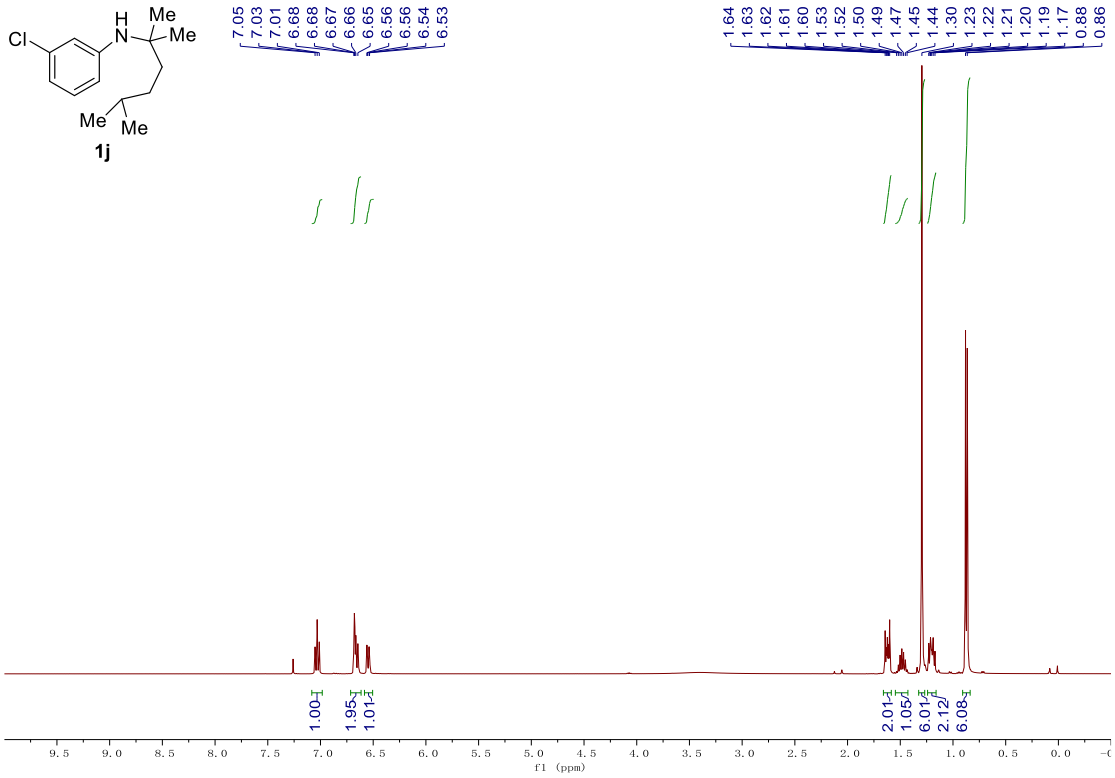

158.23 155.88 142.96 120.05 119.97 115.51 115.29 54.33 39.74 33.23 28.63 28.41 22.83
H N Me Me F Me Me
1g
f1 (ppm)

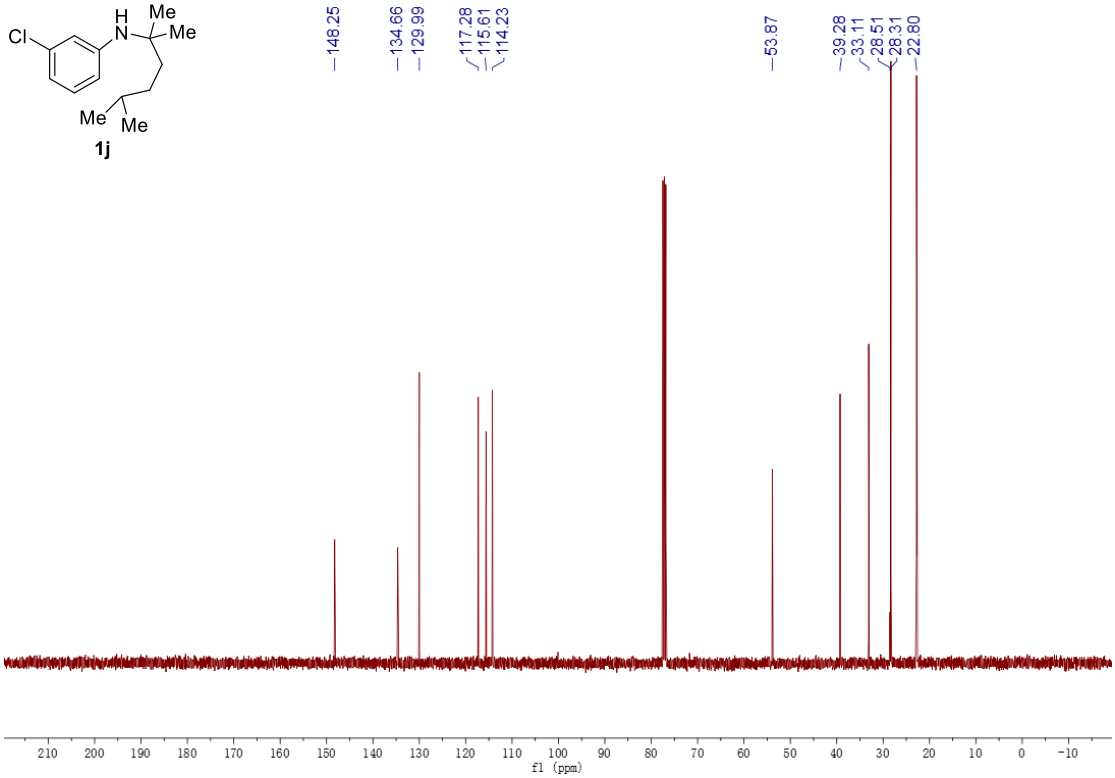

H
N
Me
Me
Cl
Me
Me
1h
7.10
7.09
7.09
7.07
7.07
7.06
6.64
6.62
3.03
1.61
1.60
1.59
1.58
1.57
1.52
1.50
1.49
1.47
1.45
1.44
1.42
1.41
1.27
1.23
1.21
1.21
1.20
1.20
1.18
1.17
0.87
0.85
2.00
2.01
1.10
2.15
1.18
6.10
2.23
6.25
f1 (ppm)

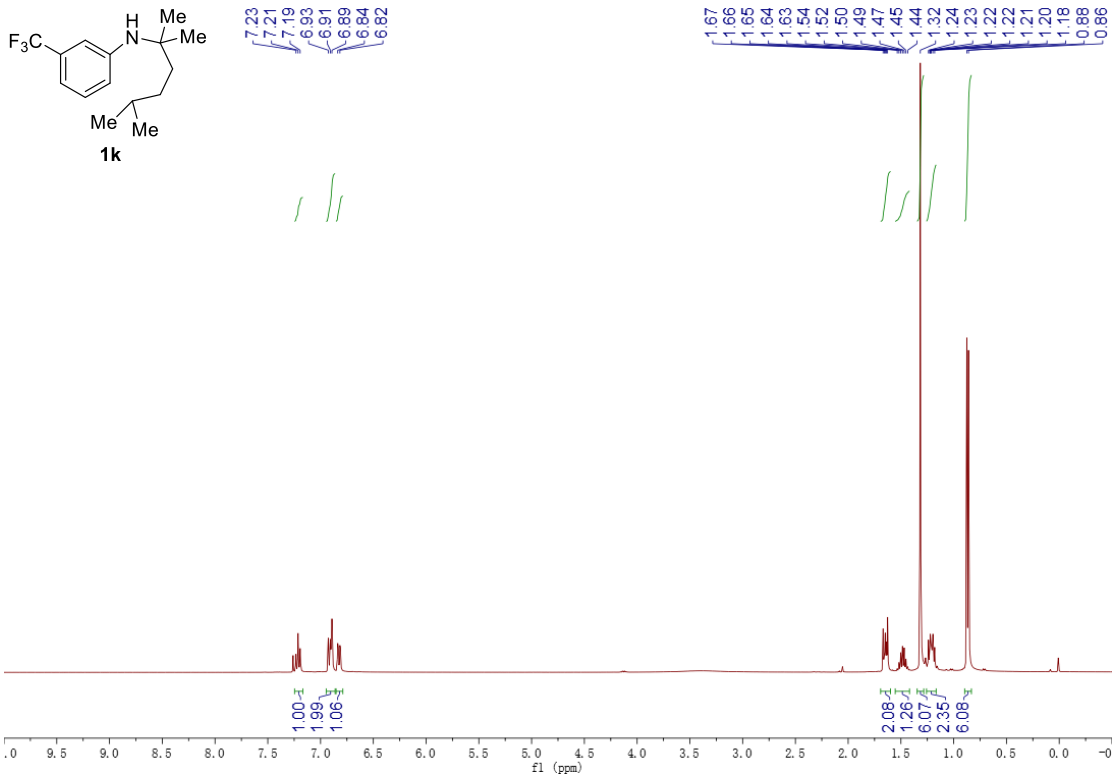

H
N
Me
Me
Cl
Me
Me
1h
145.57
128.88
122.68
117.93
53.99
39.34
33.15
28.55
28.35
22.81
f1 (ppm)

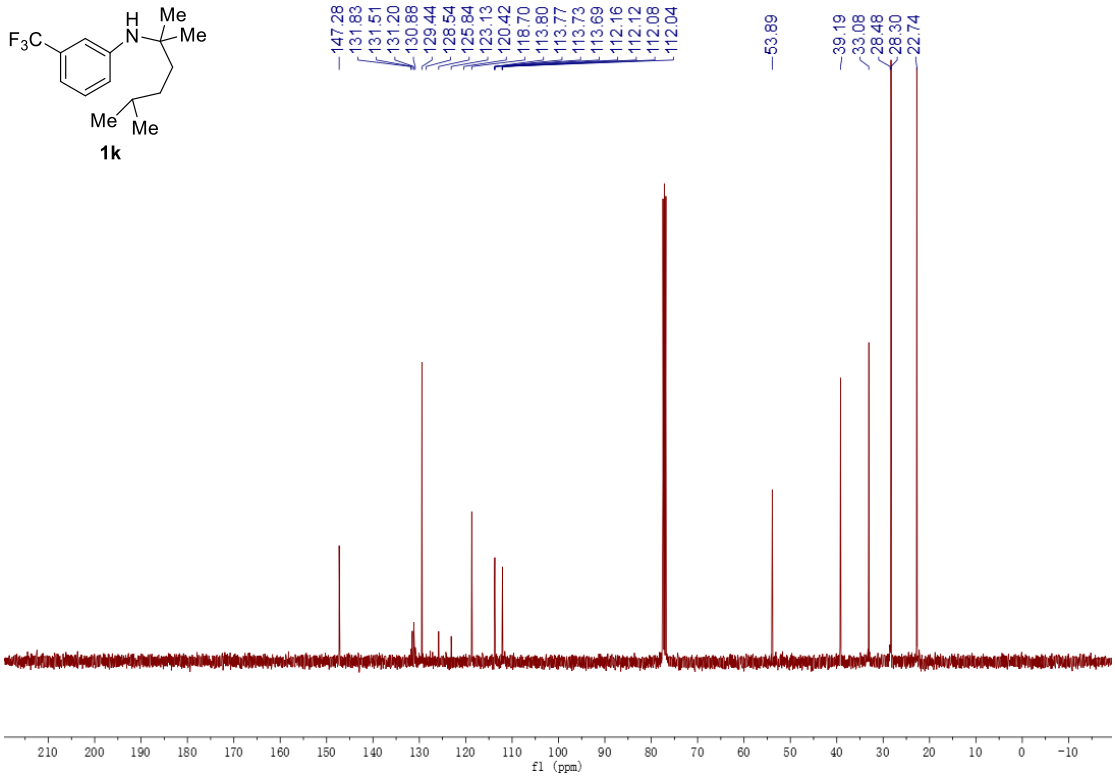

Me
H
N
Me
Me
Me
Me
1i
7.06
7.04
7.02
6.56
6.56
6.54
2.87
2.27
1.63
1.62
1.61
1.60
1.59
1.52
1.50
1.49
1.47
1.45
1.28
1.26
1.25
1.24
1.24
1.23
1.23
1.22
1.22
1.21
1.20
0.89
0.87
1.00
2.98
1.12
3.01
2.02
1.02
5.94
2.27
6.00
f1 (ppm)

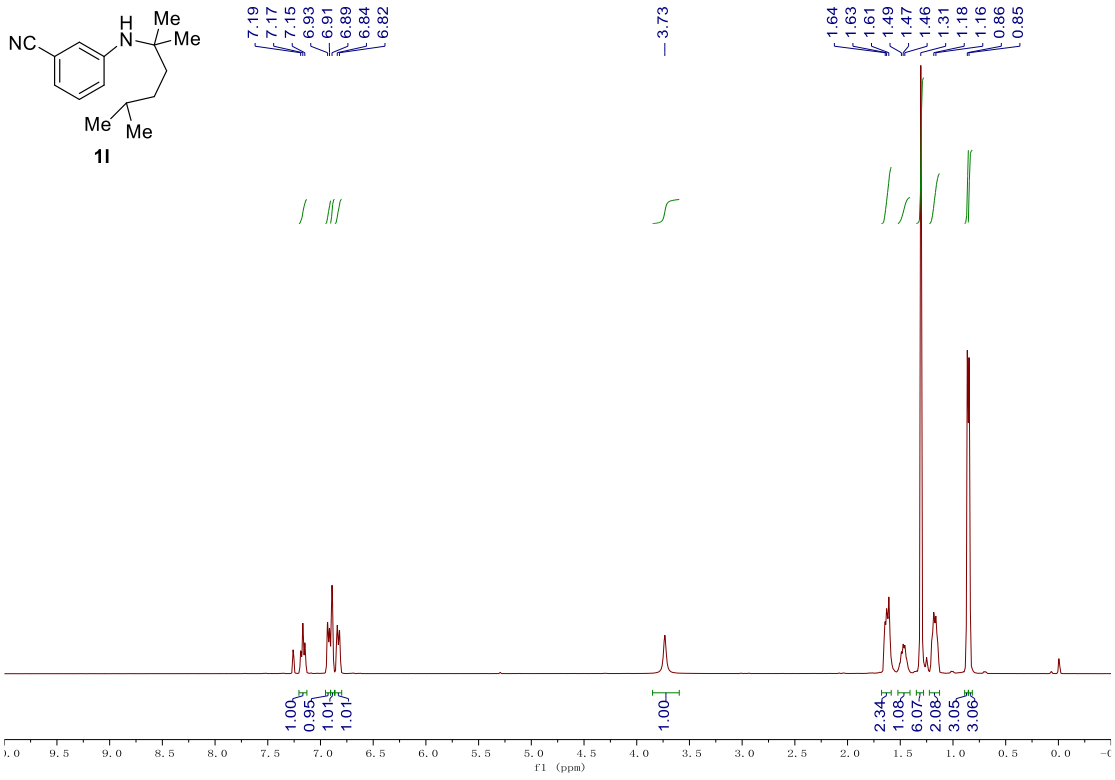

Me
H
N
Me
Me
Me
Me
1i
147.00
138.69
128.87
118.95
117.99
114.03
53.82
39.77
33.22
28.61
28.42
22.83
21.78
f1 (ppm)

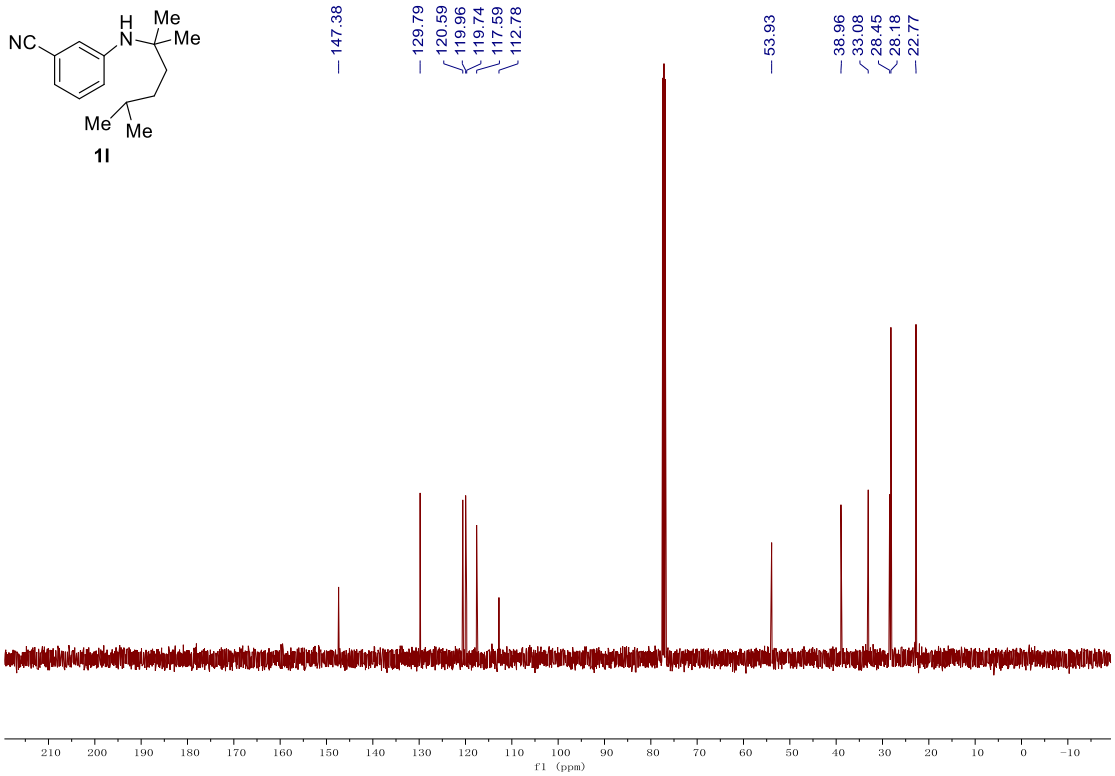

Cl
H
N
Me
Me
Me
Me
1j
7.05
7.03
7.01
6.68
6.68
6.67
6.66
6.65
6.56
6.56
6.54
6.53
1.64
1.63
1.62
1.61
1.60
1.53
1.52
1.50
1.49
1.47
1.45
1.44
1.30
1.23
1.22
1.21
1.20
1.19
1.17
0.88
0.86
1.00
1.95
1.01
2.01
1.05
6.01
2.12
6.08
f1 (ppm)

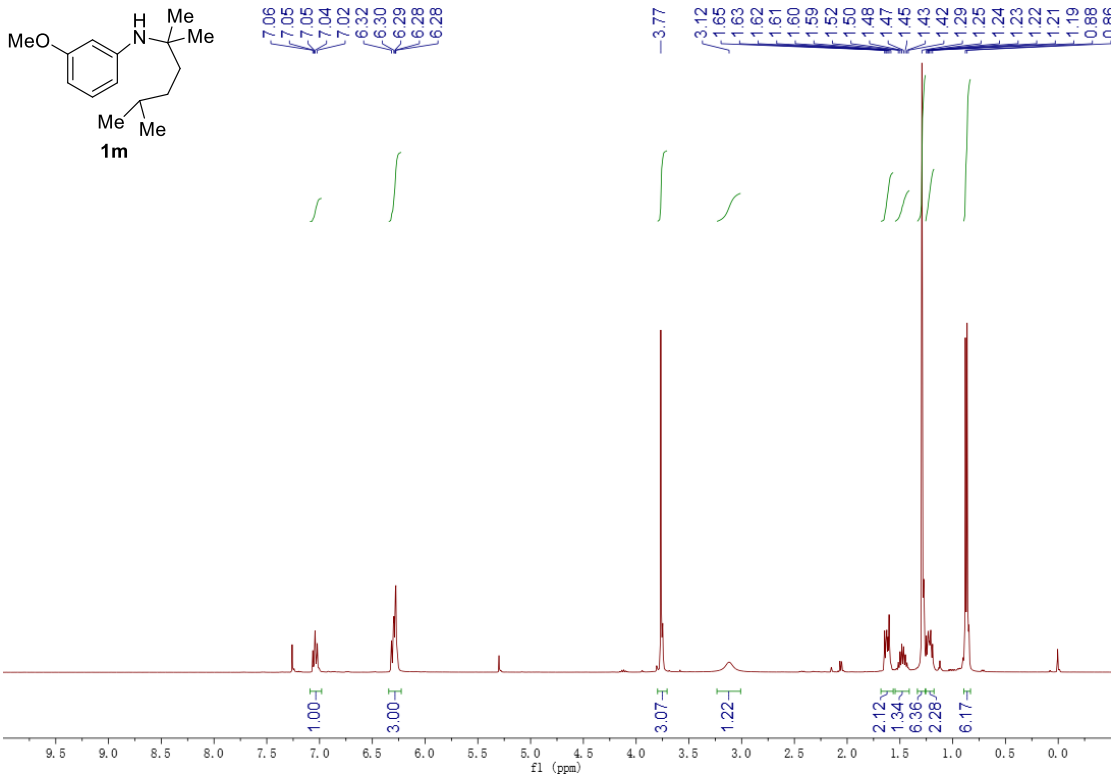

Cl
H
N
Me
Me
Me
Me
1j
148.25
134.66
129.99
117.28
115.61
114.23
53.87
39.28
33.11
28.51
28.31
22.80
f1 (ppm)

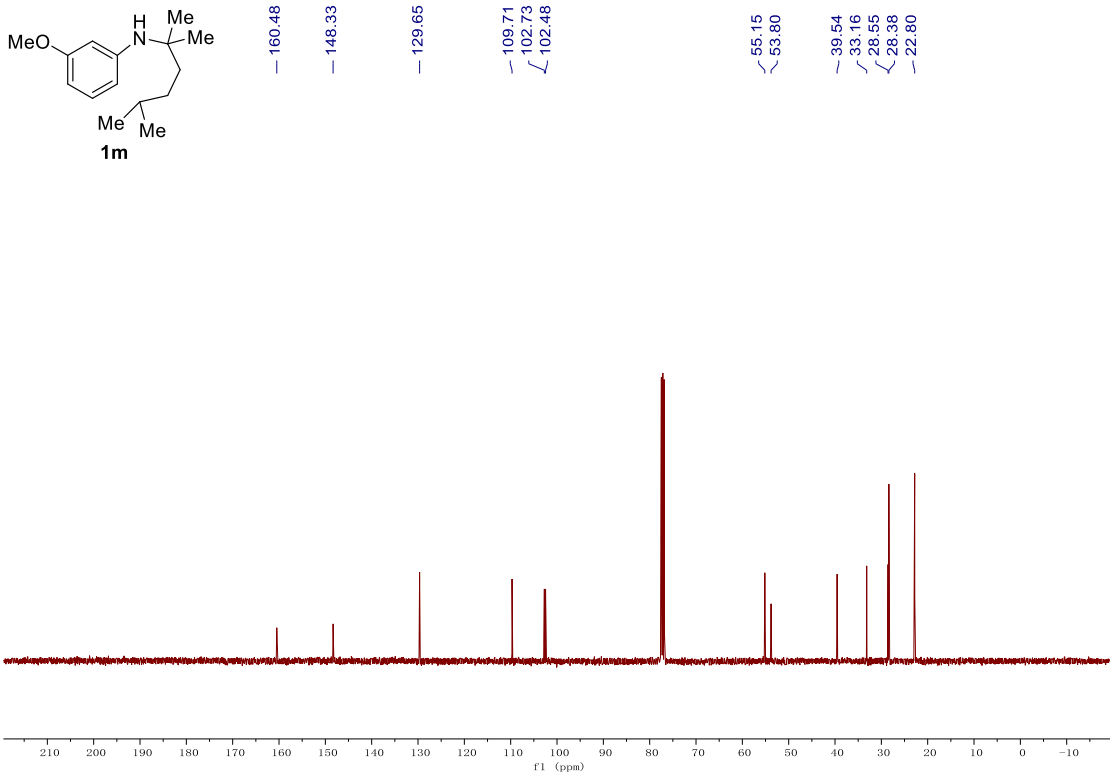

F3C
H
N
Me
Me
Me
Me
1k
7.23
7.21
7.19
6.93
6.91
6.89
6.84
6.82
1.67
1.66
1.65
1.64
1.63
1.54
1.52
1.50
1.49
1.47
1.45
1.44
1.32
1.24
1.23
1.22
1.22
1.21
1.20
1.18
0.88
0.86
1.00
1.99
1.06
2.08
1.26
6.07
2.35
6.08
f1 (ppm)

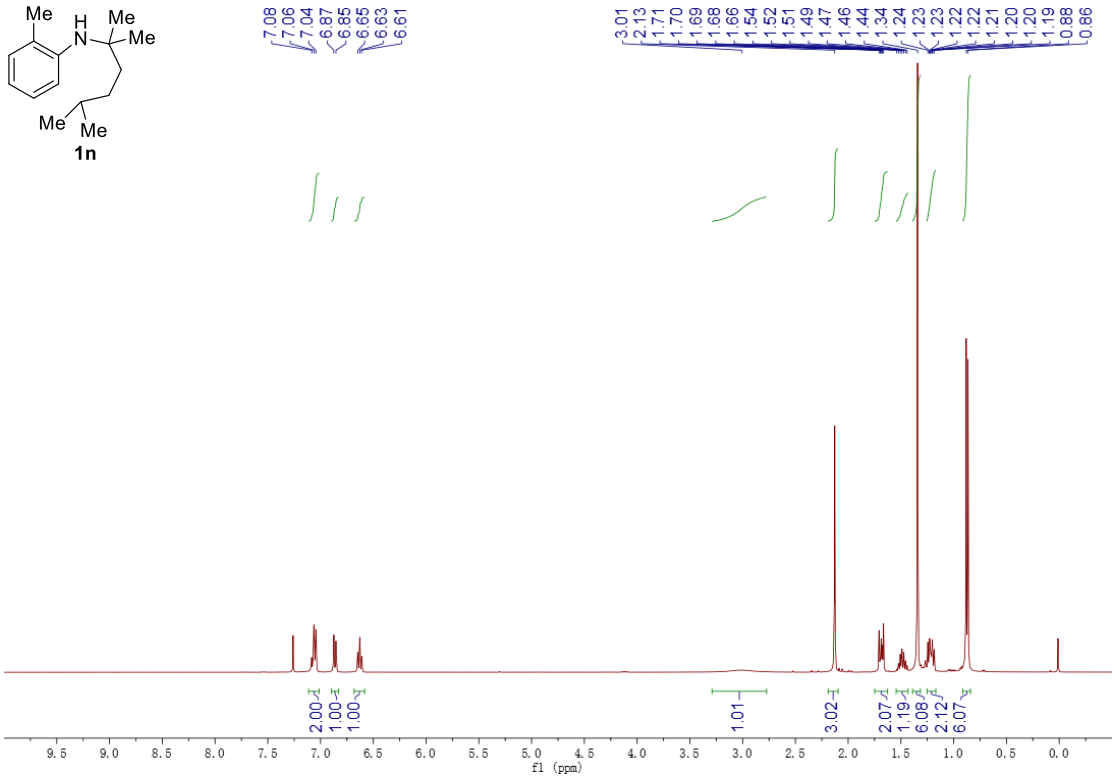

F3C
H
N
Me
Me
Me
Me
1k
147.28
131.83
131.51
131.20
130.88
129.44
128.54
125.84
123.13
120.42
118.70
113.80
113.77
113.73
113.69
112.16
112.12
112.08
112.04
53.89
39.19
33.08
28.48
28.30
22.74
f1 (ppm)

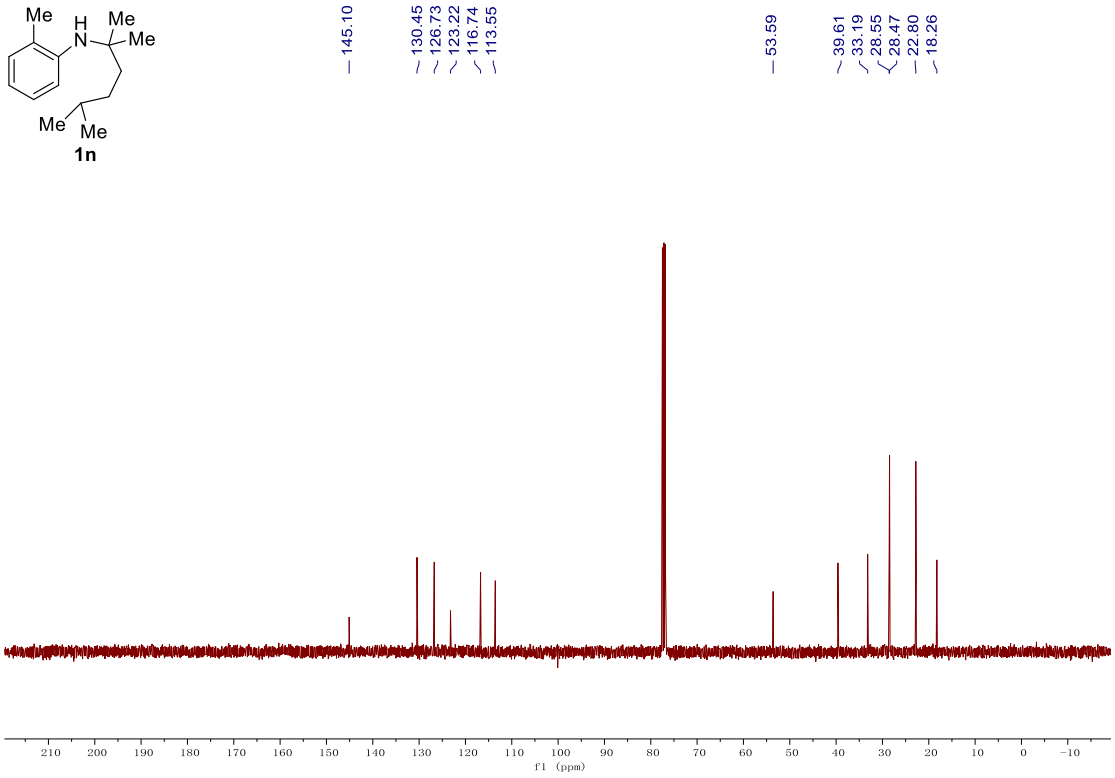

NC
H
N
Me
Me
Me
Me
1l
7.19
7.17
7.15
6.93
6.91
6.89
6.84
6.82
3.73
1.64
1.63
1.61
1.49
1.47
1.46
1.31
1.18
1.16
0.86
0.85
1.00
0.95
1.01
1.01
1.00
2.34
1.08
6.07
2.08
3.05
3.06
f1 (ppm)

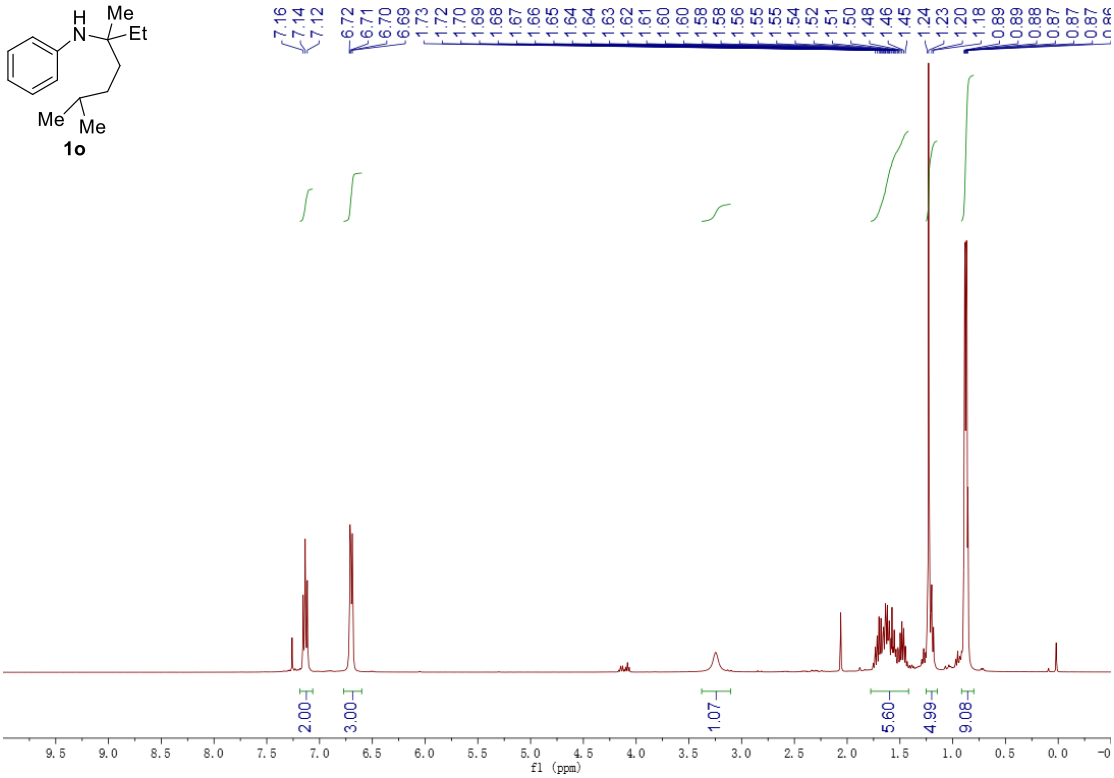

NC
H
N
Me
Me
Me
Me
1l
147.38
129.79
120.59
119.96
119.74
117.59
112.78
53.93
38.96
33.08
28.45
28.18
22.77
f1 (ppm)

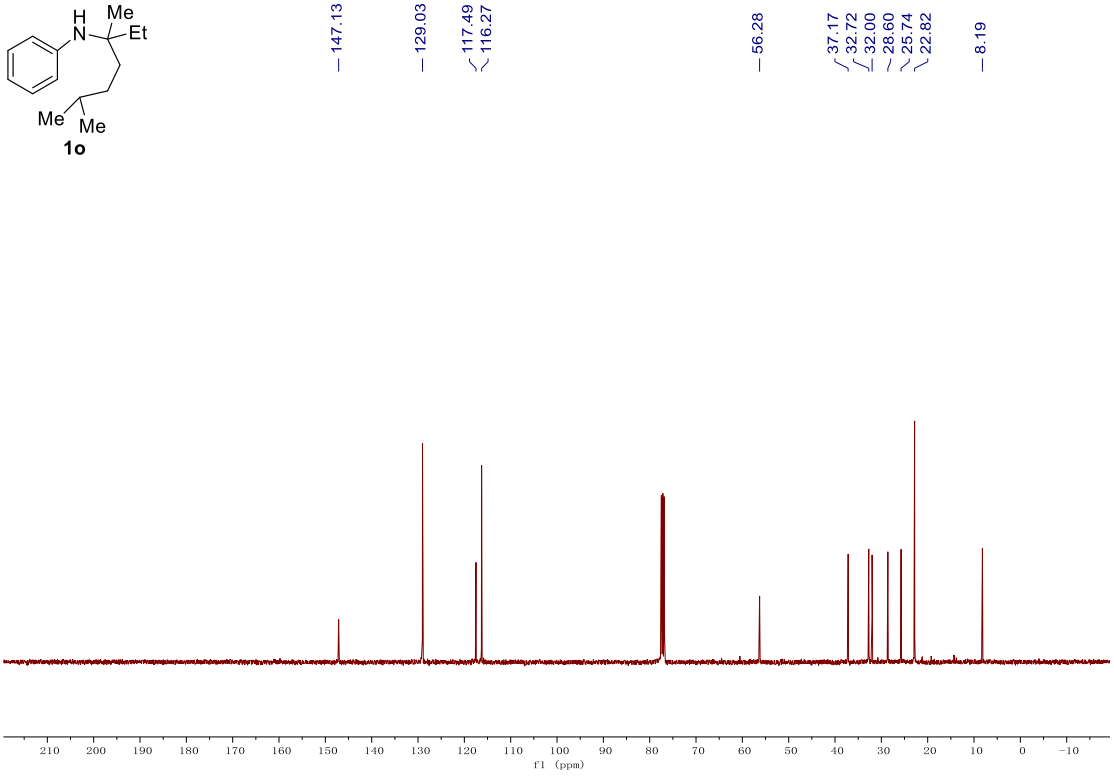

MeO
H
N
Me
Me
Me
Me
1m
7.06
7.05
7.05
7.04
7.02
6.32
6.30
6.29
6.28
6.28
3.77
3.12
1.65
1.63
1.62
1.61
1.60
1.59
1.52
1.50
1.48
1.47
1.45
1.43
1.42
1.29
1.25
1.24
1.23
1.22
1.21
1.19
0.88
1.00
3.00
3.07
1.22
2.12
1.34
6.36
2.28
6.17
f1 (ppm)

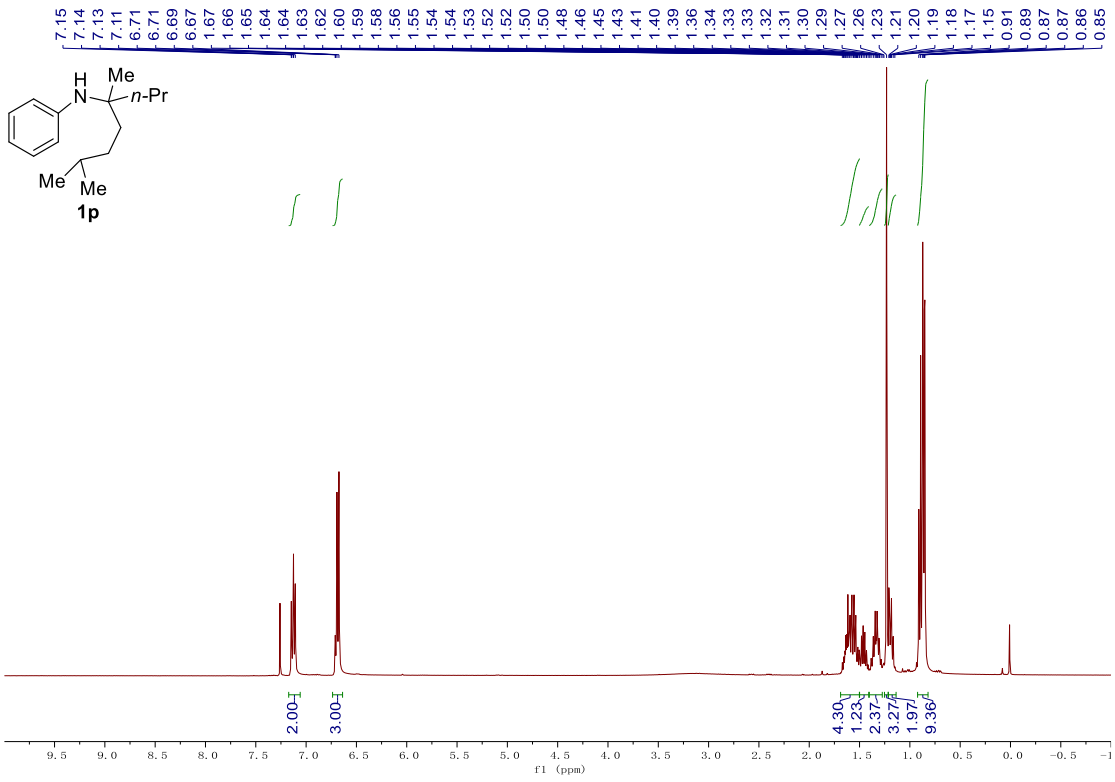

MeO
H
N
Me
Me
Me
Me
1m
160.48
148.33
129.65
109.71
102.73
102.48
55.15
53.80
39.54
33.16
28.55
28.38
22.80
f1 (ppm)

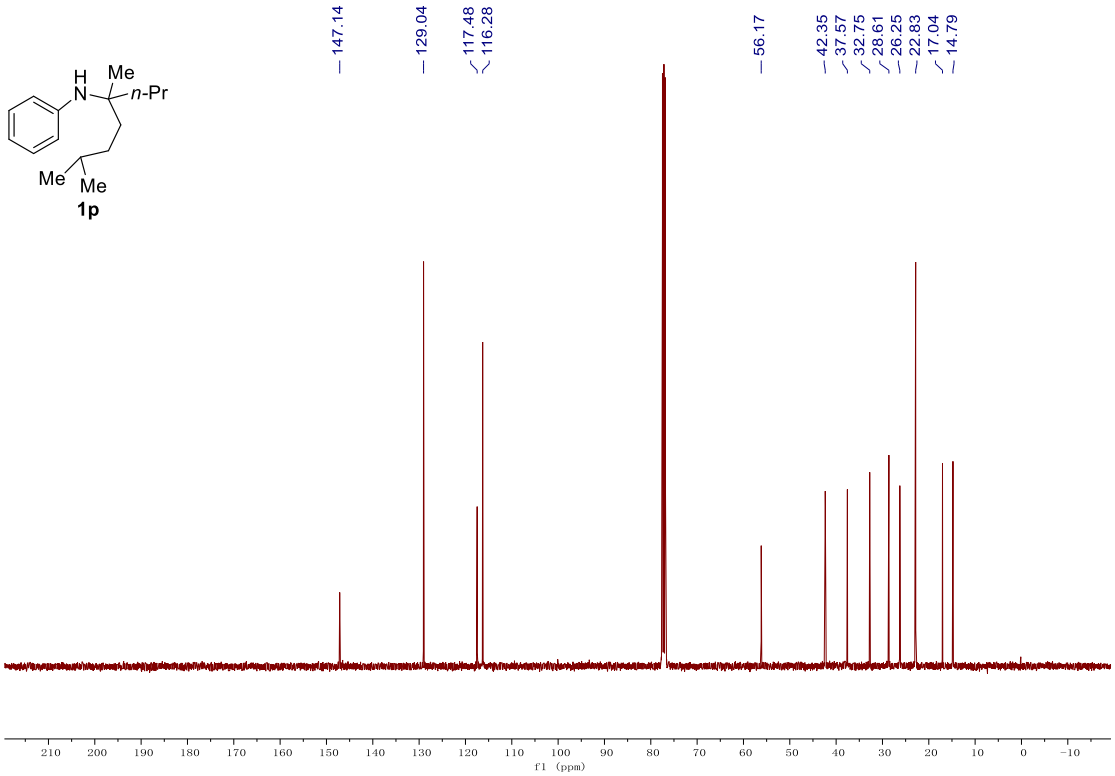

Me
H
N
Me
Me
Me
Me
1n
7.08
7.06
7.04
6.87
6.85
6.65
6.63
6.61
3.01
2.13
1.71
1.70
1.69
1.68
1.66
1.54
1.52
1.51
1.49
1.47
1.46
1.44
1.34
1.24
1.23
1.23
1.22
1.22
1.21
1.20
1.20
1.19
0.88
0.86
2.00
1.00
1.00
1.01
3.02
2.07
1.19
6.08
2.12
6.07
f1 (ppm)

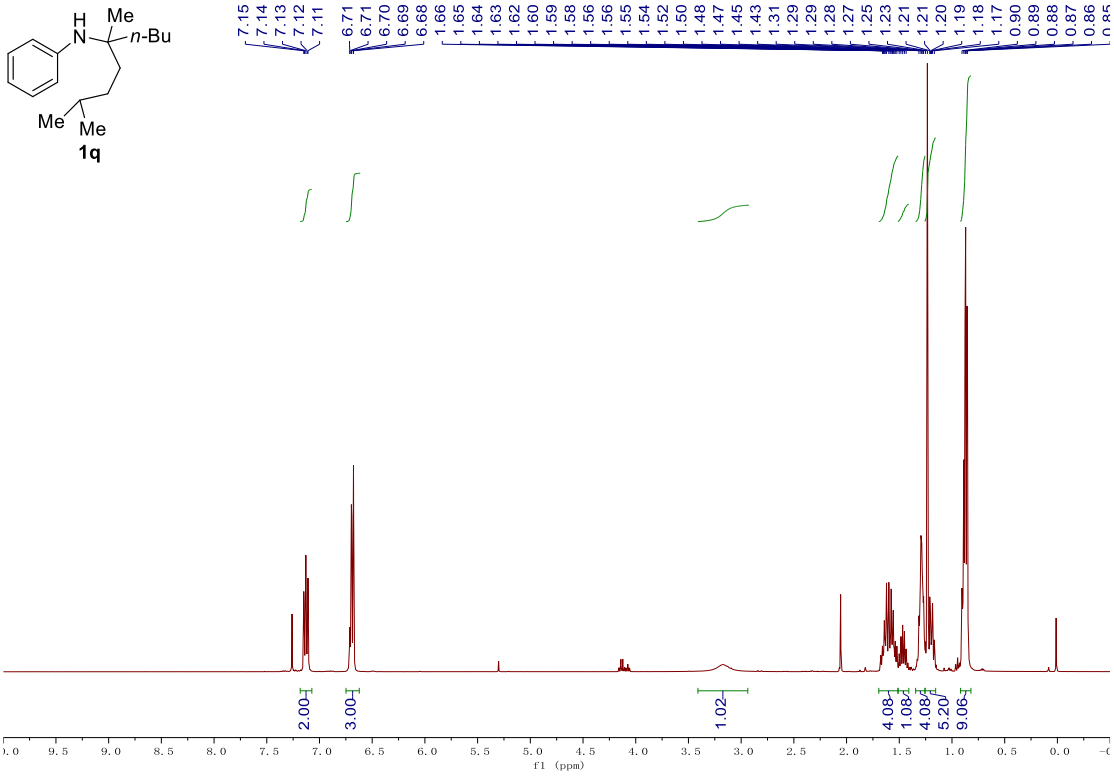

Me
H
N
Me
Me
Me
Me
1n
145.10
130.45
126.73
123.22
116.74
113.55
53.59
39.61
33.19
28.55
28.47
22.80
18.26
f1 (ppm)

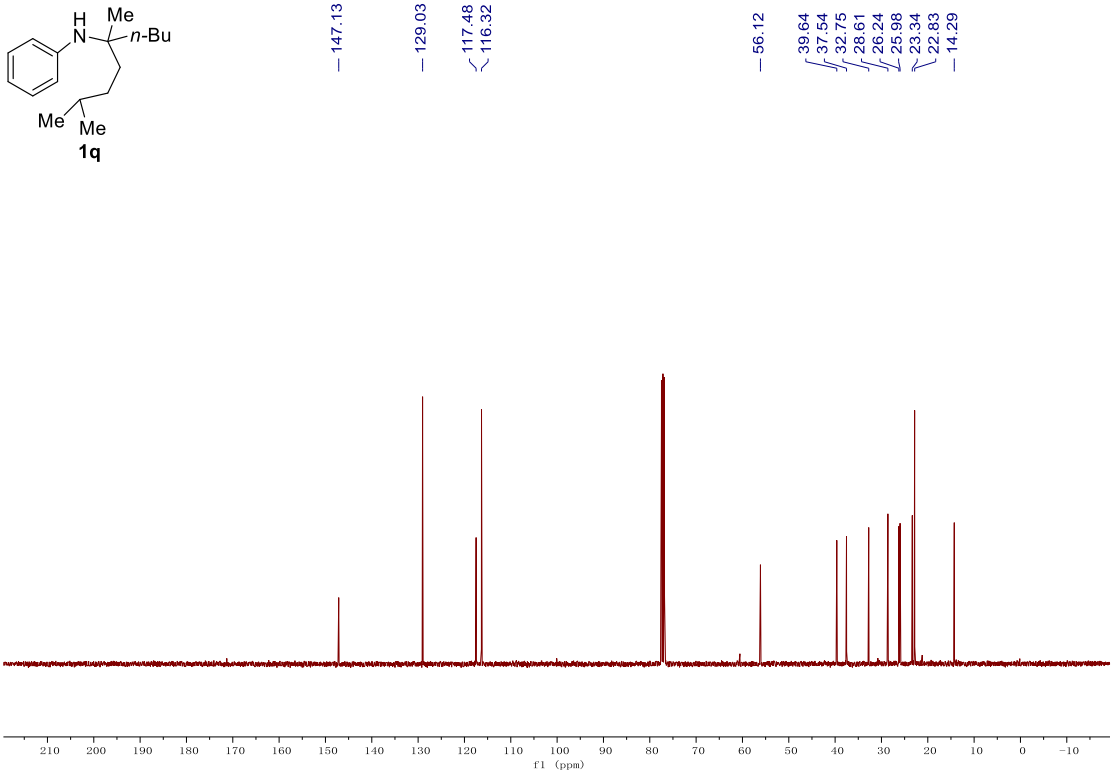

Me
H
N
Et
Me
Me
1o
7.16
7.14
7.12
6.72
6.71
6.70
6.69
1.73
1.72
1.70
1.69
1.68
1.67
1.66
1.65
1.64
1.64
1.63
1.62
1.61
1.60
1.60
1.58
1.58
1.56
1.55
1.55
1.54
1.52
1.51
1.50
1.48
1.46
1.45
1.24
1.23
1.20
1.18
0.89
0.89
0.88
0.87
0.87
0.87
2.00
3.00
1.07
5.60
4.99
9.08
f1 (ppm)

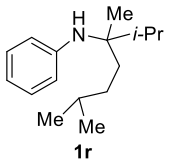

Me
H
N
Et
Me
Me
1o
147.13
129.03
117.49
116.27
56.28
37.17
32.72
32.00
28.60
25.74
22.82
8.19
f1 (ppm)


7.15 7.14 7.13 7.11 6.71 6.71 6.69 6.67 1.67 1.66 1.65 1.64 1.64 1.63 1.62 1.60 1.59 1.58 1.56 1.55 1.54 1.54 1.53 1.52 1.52 1.50 1.50 1.48 1.46 1.45 1.43 1.41 1.40 1.39 1.36 1.34 1.33 1.33 1.32 1.31 1.30 1.29 1.27 1.26 1.23 1.21 1.20 1.19 1.18 1.17 1.15 0.91 0.89 0.87 0.87 0.86 0.85
H
N
Me
n-Pr
Me
Me
1p
2.00
3.00
4.30
1.23
2.37
3.27
1.97
9.36
f1 (ppm)


147.14
129.04
117.48
116.28
56.17
42.35
37.57
32.75
28.61
26.25
22.83
17.04
14.79
H
N
Me
n-Pr
Me
Me
1p
f1 (ppm)

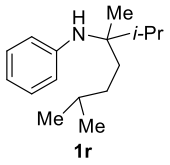

Me
H
N
n-Bu
Me
Me
1q
7.15
7.14
7.13
7.12
7.11
6.71
6.71
6.70
6.69
6.68
1.66
1.65
1.64
1.63
1.62
1.60
1.59
1.58
1.56
1.56
1.55
1.54
1.52
1.50
1.48
1.47
1.45
1.43
1.31
1.29
1.29
1.28
1.27
1.25
1.23
1.21
1.21
1.20
1.19
1.18
1.17
0.90
0.89
0.88
0.87
0.86
2.00
3.00
1.02
4.08
1.08
4.08
5.20
9.06
f1 (ppm)


Me
H
N
n-Bu
Me
Me
1q
147.13
129.03
117.48
116.32
56.12
39.64
37.54
32.75
28.61
26.24
25.98
23.34
22.83
14.29
f1 (ppm)


H
N
Me
i-Pr
Me
Me

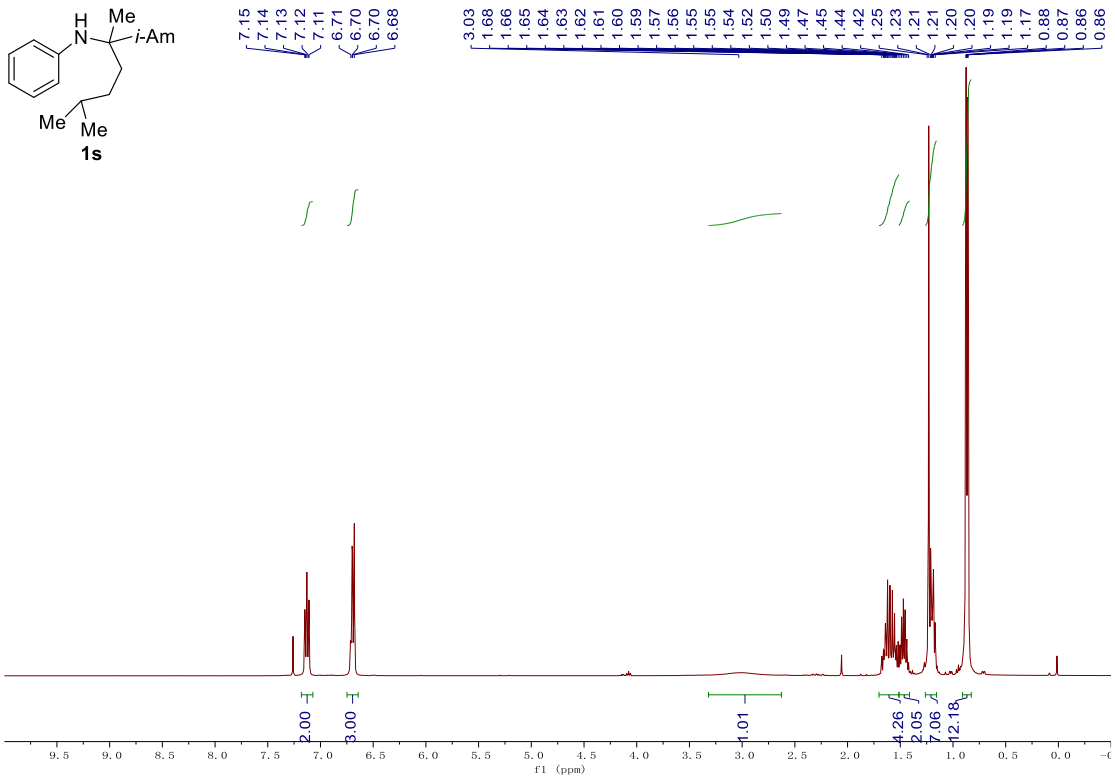
1r

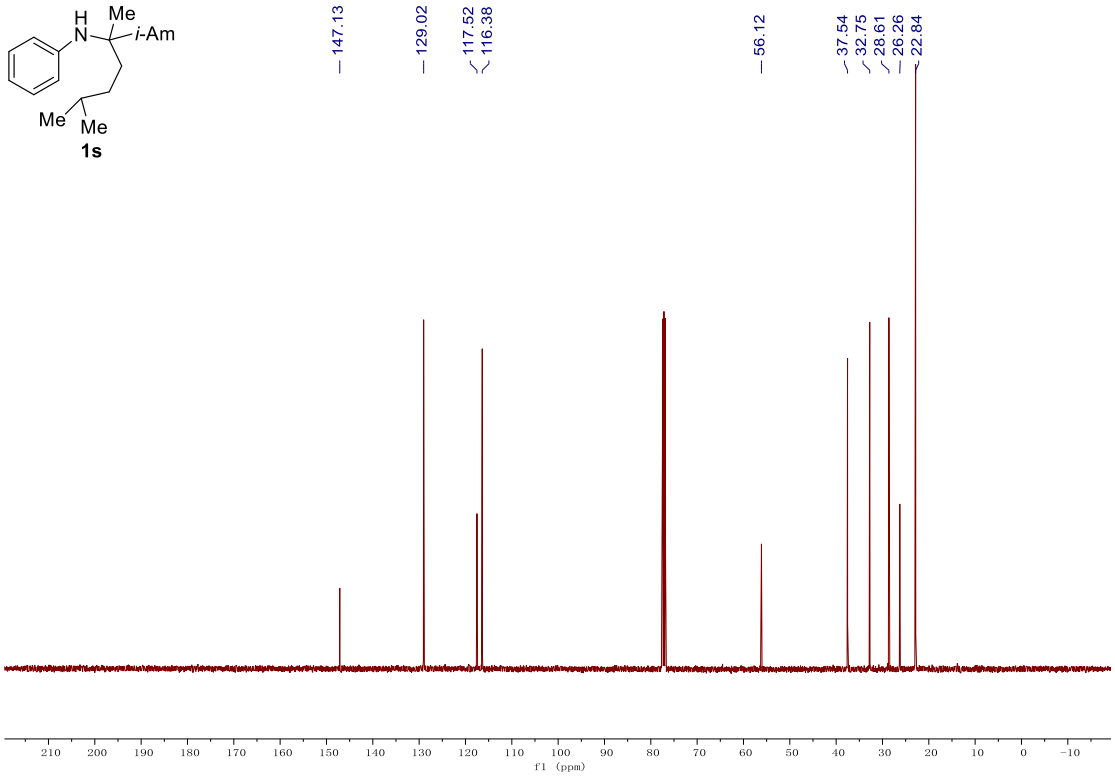
7.15
7.13
7.11
6.69
6.69
6.68
6.67
6.66
2.20
2.18
2.17
2.15
1.74
1.73
1.72
1.71
1.70
1.68
1.64
1.62
1.61
1.60
1.59
1.58
1.56
1.50
1.49
1.47
1.45
1.44
1.28
1.26
1.24
1.24
1.23
1.22
1.21
1.20
1.20
1.14
0.93
0.92
0.90
0.87
2.00
2.99
1.01
1.03
1.03
1.05
2.22
2.99
12.20
f1 (ppm)

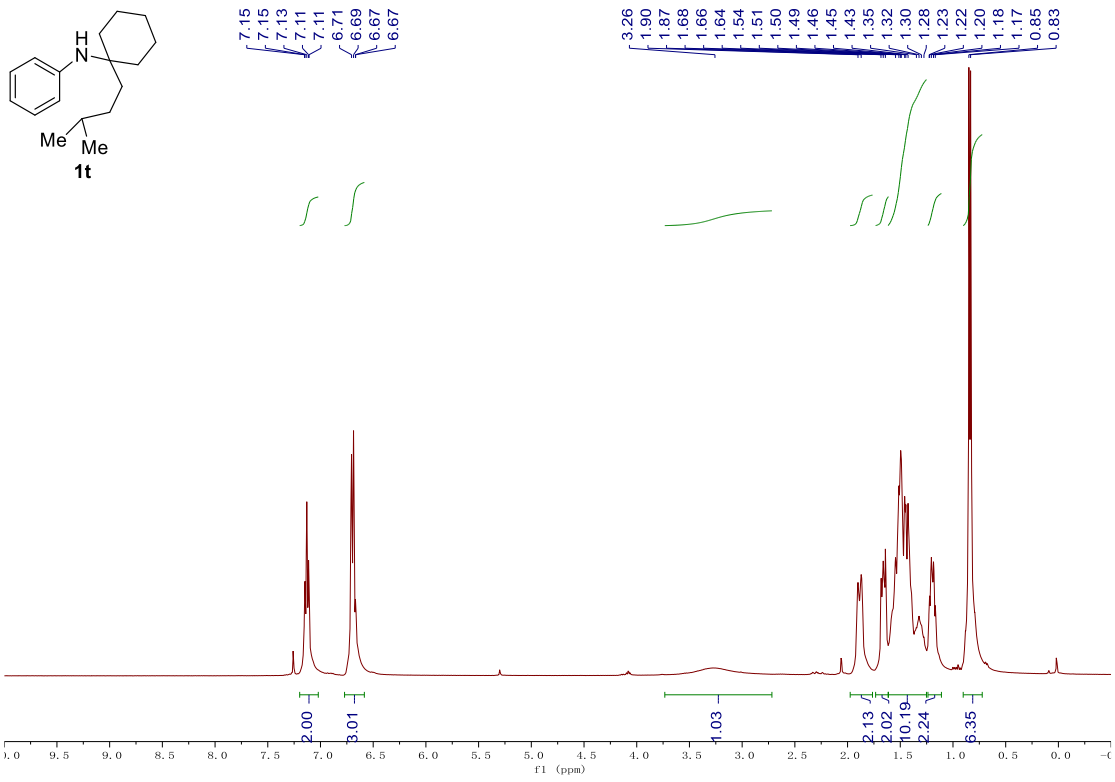

H
N
Me
i-Pr
Me
Me

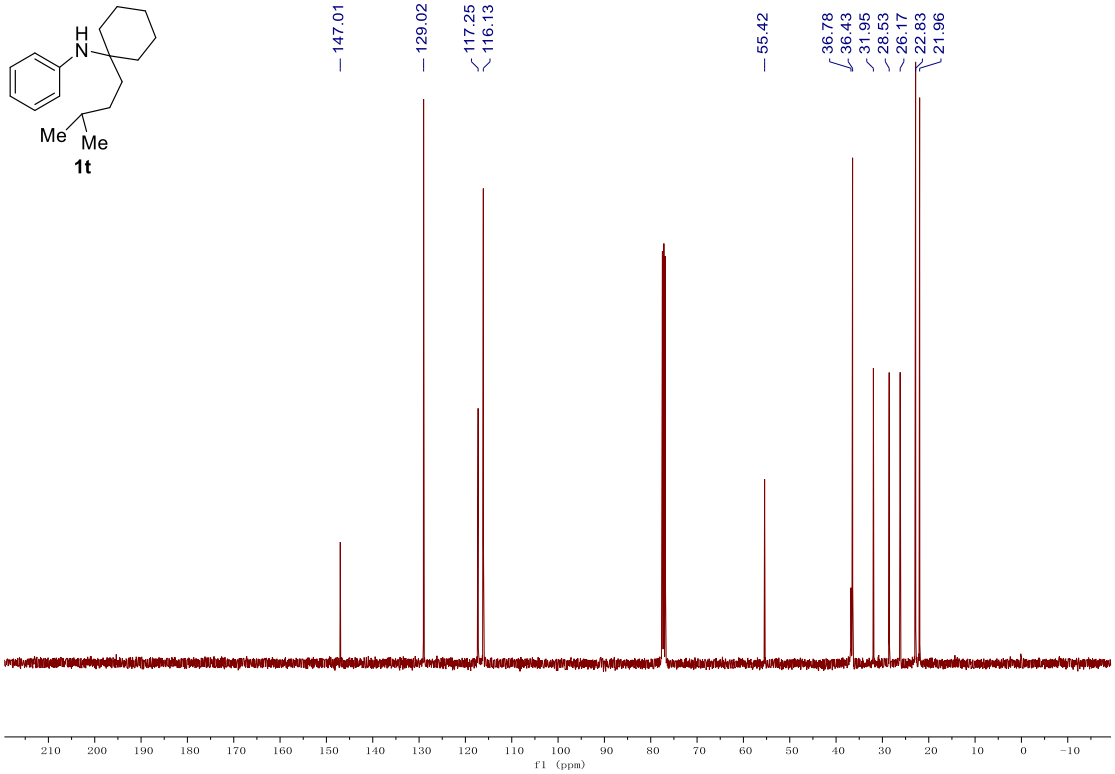
1r

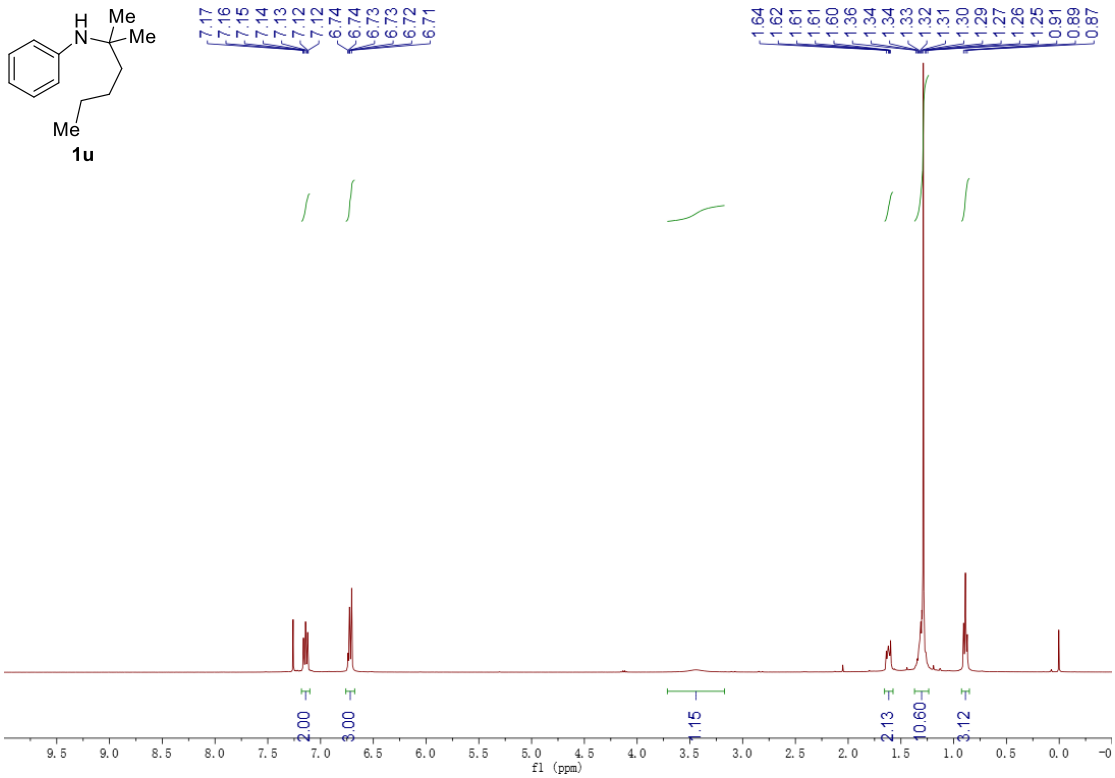
147.24
129.05
117.15
115.95
58.79
35.14
34.46
32.56
28.66
22.92
22.80
21.81
17.75
17.31
f1 (ppm)

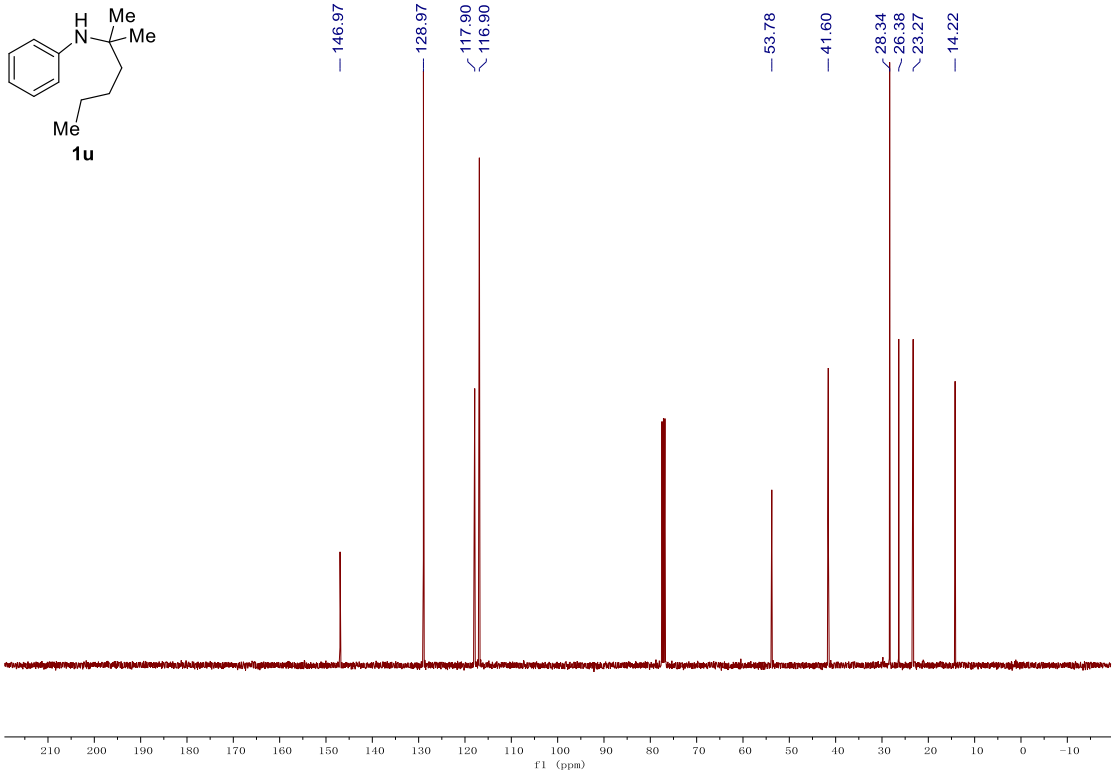

H
N
Me
i-Am
Me
Me
1s
7.15
7.14
7.13
7.12
7.11
6.71
6.70
6.70
6.68
3.03
1.68
1.66
1.65
1.64
1.63
1.62
1.61
1.60
1.59
1.57
1.56
1.55
1.55
1.54
1.52
1.50
1.49
1.47
1.45
1.44
1.42
1.25
1.23
1.21
1.21
1.20
1.20
1.19
1.19
1.17
0.88
0.87
0.86
0.86
2.00
3.00
1.01
4.26
2.05
7.06
12.18
f1 (ppm)

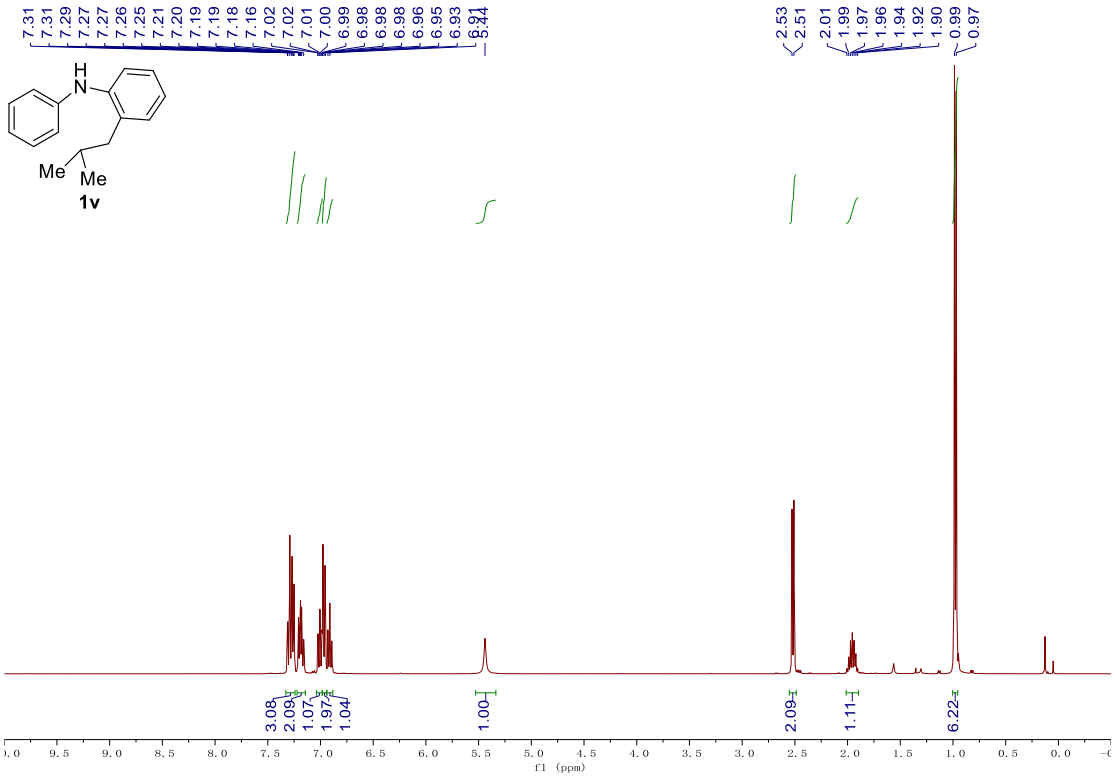

H
N
Me
i-Am
Me
Me
1s
147.13
129.02
117.52
116.38
56.12
37.54
32.75
28.61
26.26
22.84
f1 (ppm)

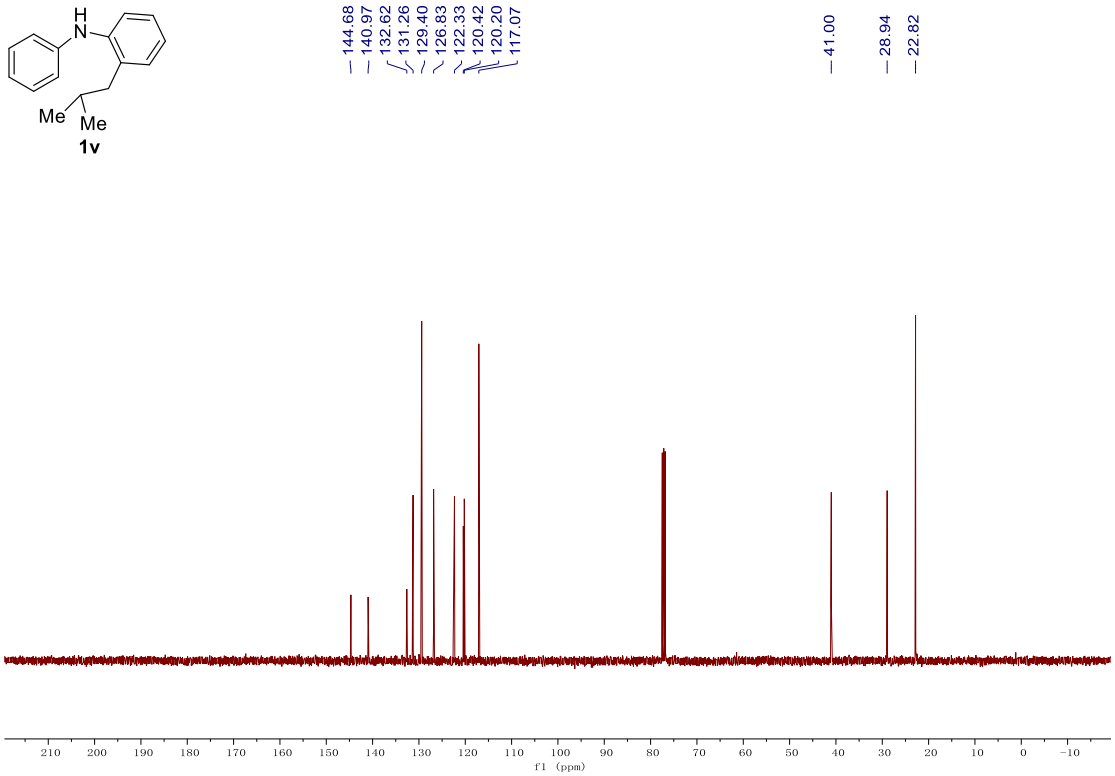

H
N
Me
Me
1t
7.15
7.15
7.13
7.11
7.11
6.71
6.69
6.67
6.67
3.26
1.90
1.87
1.68
1.66
1.64
1.54
1.51
1.50
1.49
1.46
1.45
1.43
1.35
1.32
1.30
1.28
1.23
1.22
1.20
1.18
1.17
0.85
0.83
2.00
3.01
1.03
2.13
2.02
10.19
2.24
6.35
f1 (ppm)

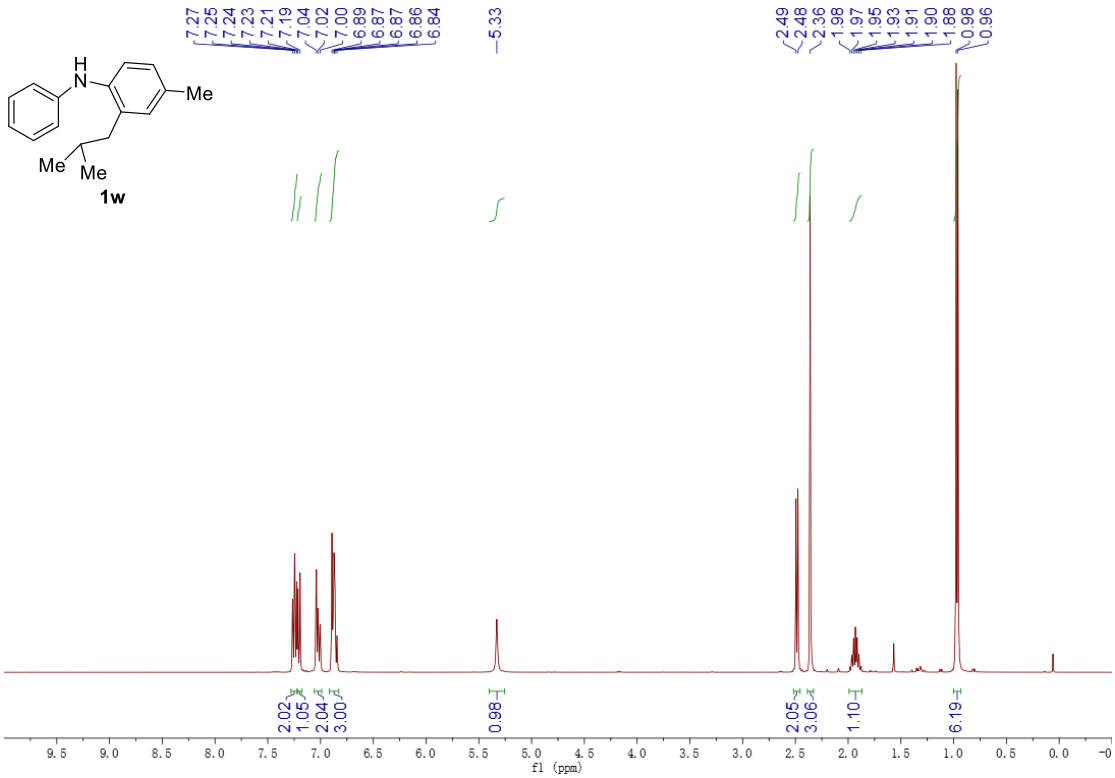

H
N
Me
Me
1t
147.01
129.02
117.25
116.13
55.42
36.78
36.43
31.95
28.53
26.17
22.83
21.96
f1 (ppm)

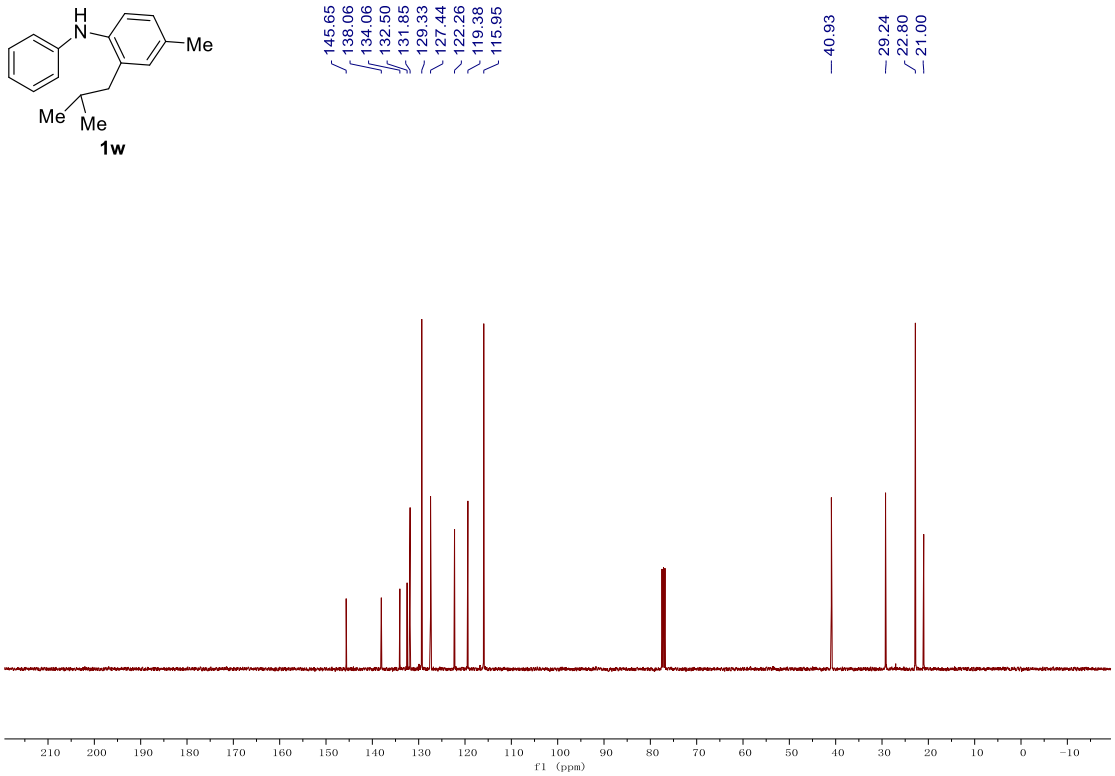

H
N
Me
Me
Me
1u
7.17
7.16
7.15
7.14
7.13
7.12
7.12
6.74
6.74
6.73
6.73
6.72
6.71
1.64
1.62
1.61
1.61
1.60
1.36
1.34
1.34
1.33
1.32
1.31
1.30
1.29
1.27
1.26
1.25
0.91
0.89
0.87
2.00
3.00
1.15
2.13
10.60
3.12
f1 (ppm)

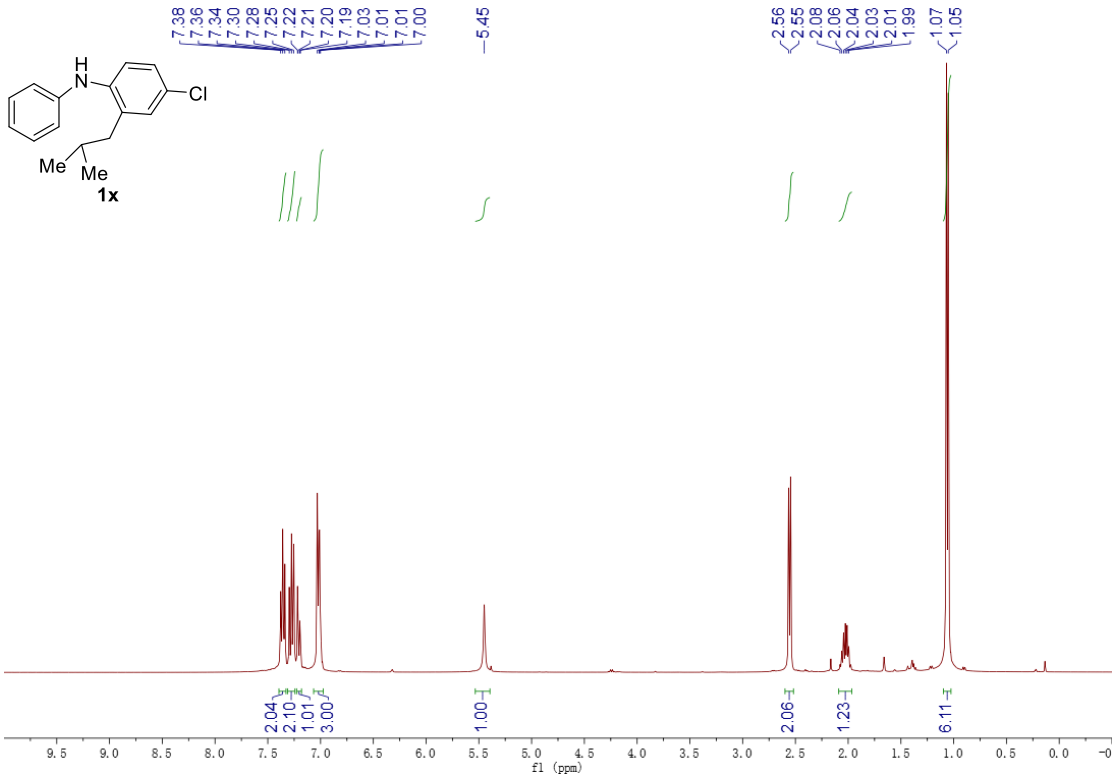

H
N
Me
Me
Me
1u
146.97
128.97
117.90
116.90
53.78
41.60
28.34
26.38
23.27
14.22
f1 (ppm)


7.31
7.31
7.29
7.27
7.27
7.26
7.25
7.21
7.20
7.19
7.19
7.18
7.16
7.02
7.02
7.01
7.00
6.99
6.98
6.98
6.98
6.96
6.95
6.93
6.91
5.44
2.53
2.51
2.01
1.99
1.97
1.96
1.94
1.92
1.90
0.99
0.97
H
N
Me
Me
1v
3.08
2.09
1.07
1.97
1.04
1.00
2.09
1.11
6.22
f1 (ppm)


144.68
140.97
132.62
131.26
129.40
126.83
122.33
120.42
120.20
117.07
41.00
28.94
22.82
H
N
Me
Me
1v
f1 (ppm)


7.27
7.25
7.24
7.23
7.21
7.19
7.04
7.02
7.00
6.89
6.87
6.87
6.86
6.84
5.33
2.49
2.48
2.36
1.98
1.97
1.95
1.93
1.91
1.90
1.88
0.98
0.96
2.02
1.05
2.04
3.00
0.98
2.05
3.06
1.10
6.19
f1 (ppm)
Me
Me
Me
1w


145.65
138.06
134.06
132.50
131.85
129.33
127.44
122.26
119.38
115.95
40.93
29.24
22.80
21.00
f1 (ppm)
Me
Me
Me
1w


7.38
7.36
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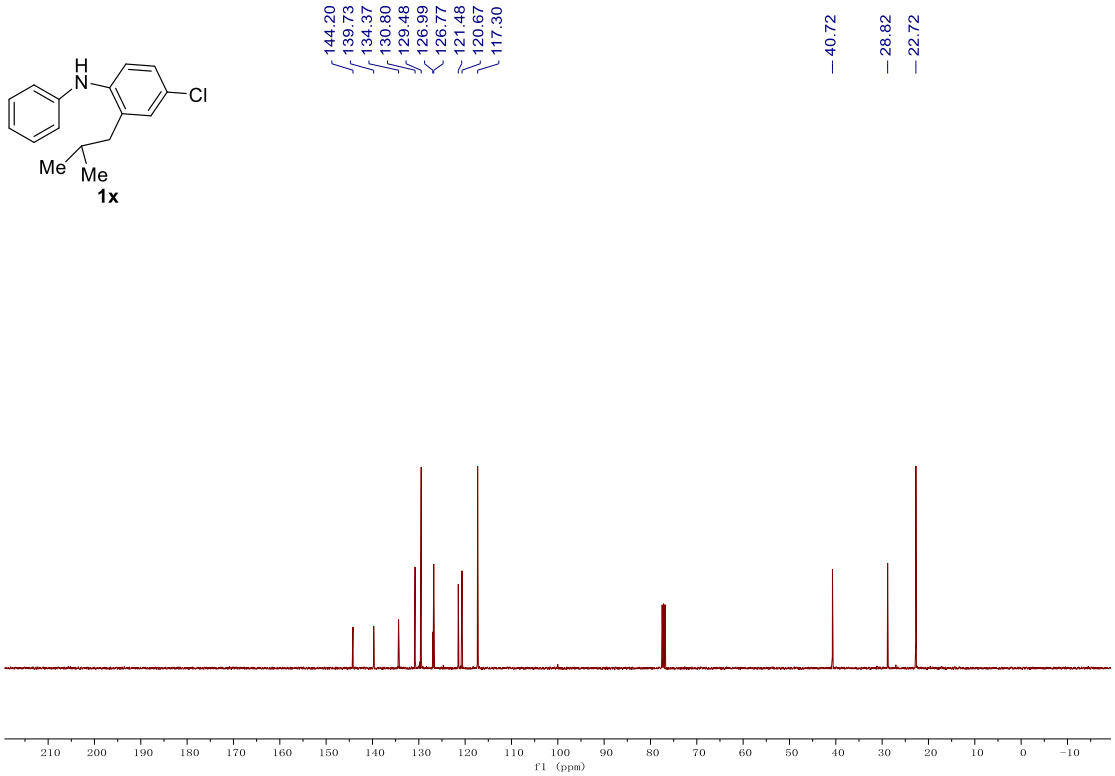
7.25
7.22
7.21
7.20
7.19
7.03
7.01
7.01
7.00
5.45
2.56
2.55
2.08
2.06
2.04
2.03
2.01
1.99
1.07
1.05
H
N
Cl
Me
Me
1x
2.04
2.10
1.01
3.00
1.00
2.06
1.23
6.11
f1 (ppm)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139.73
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130.80
129.48
126.99
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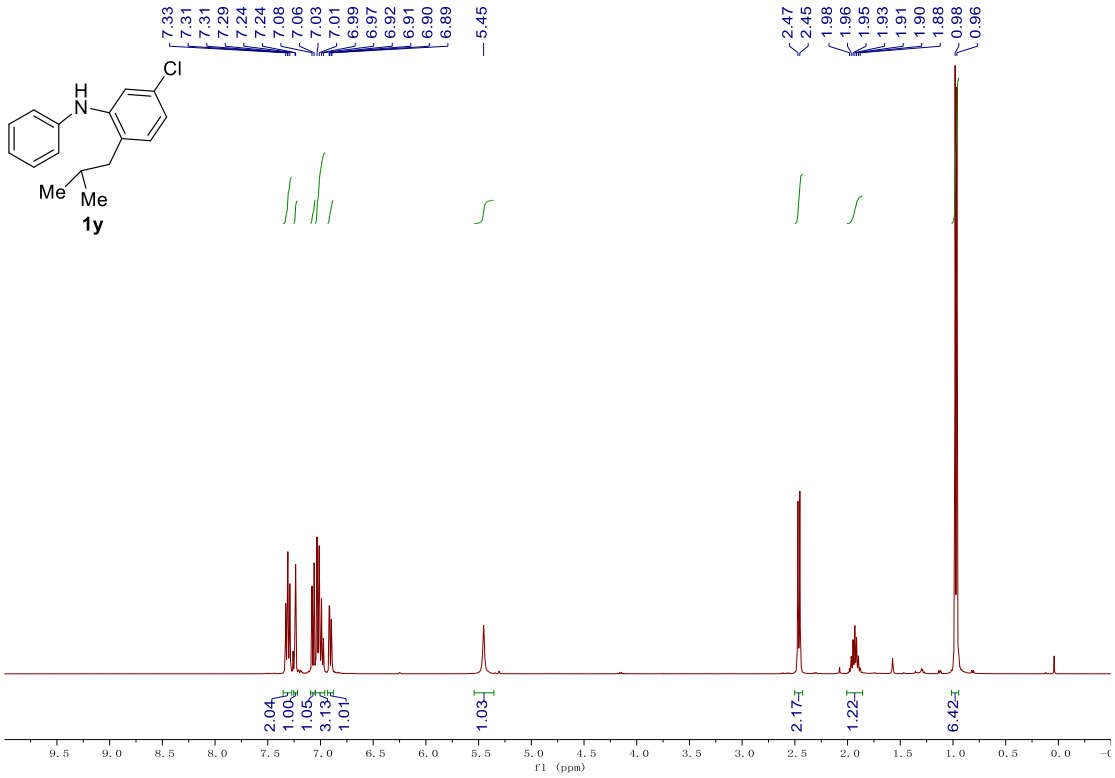
121.48
120.67
117.30
40.72
28.82
22.72
H
N
Cl
Me
Me
1x
f1 (ppm)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7.31
7.31
7.29
7.24
7.24
7.08
7.06
7.03
7.01
6.99
6.97
6.92
6.91
6.90
6.89
5.45
2.47
2.45
1.98
1.96
1.95
1.93
1.91
1.90
1.88
0.98
0.96
Cl
H
N
Me
Me
1y
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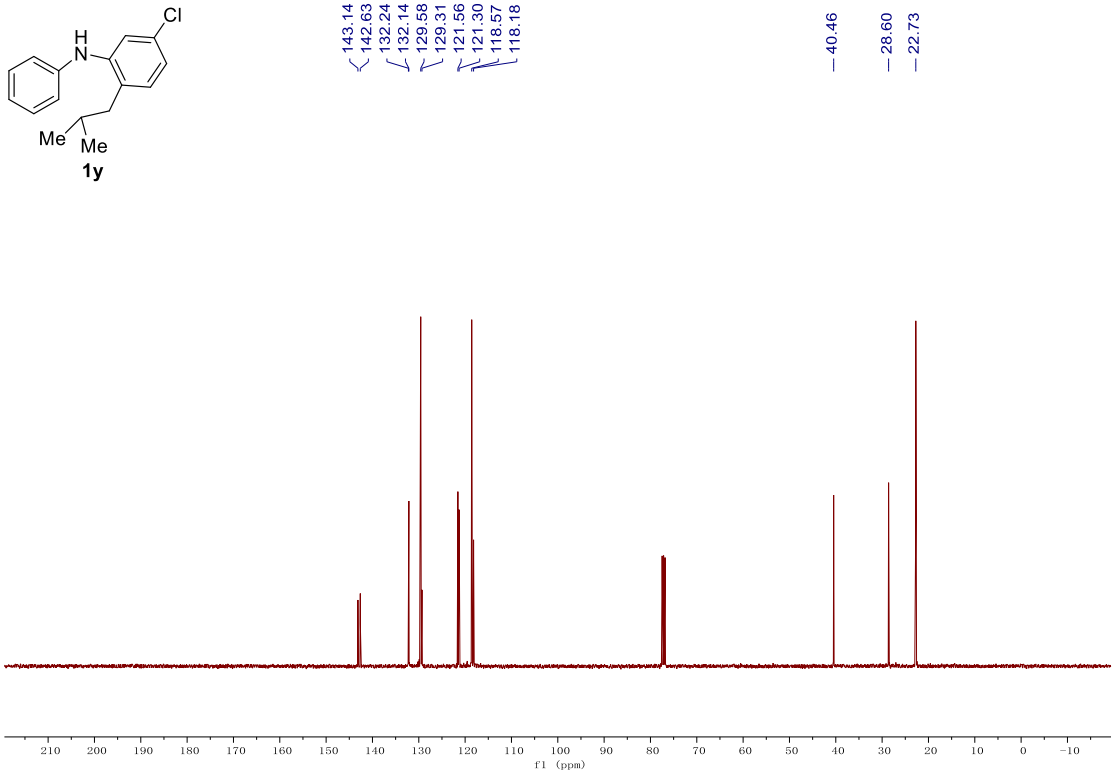
1.00
1.05
3.13
1.01
1.03
2.17
1.22
6.42
f1 (ppm)


143.14
142.63
132.24
132.14
129.58
129.31
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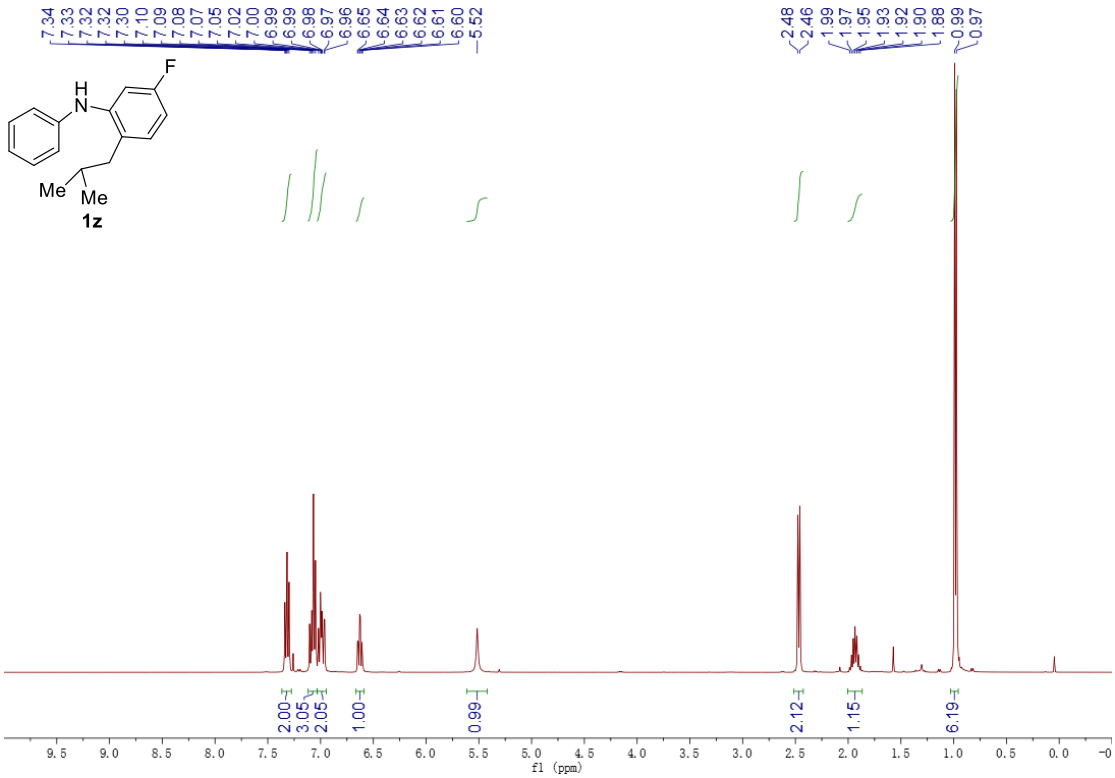
121.30
118.57
118.18
40.46
28.60
22.73
Cl
H
N
Me
Me
1y
f1 (ppm)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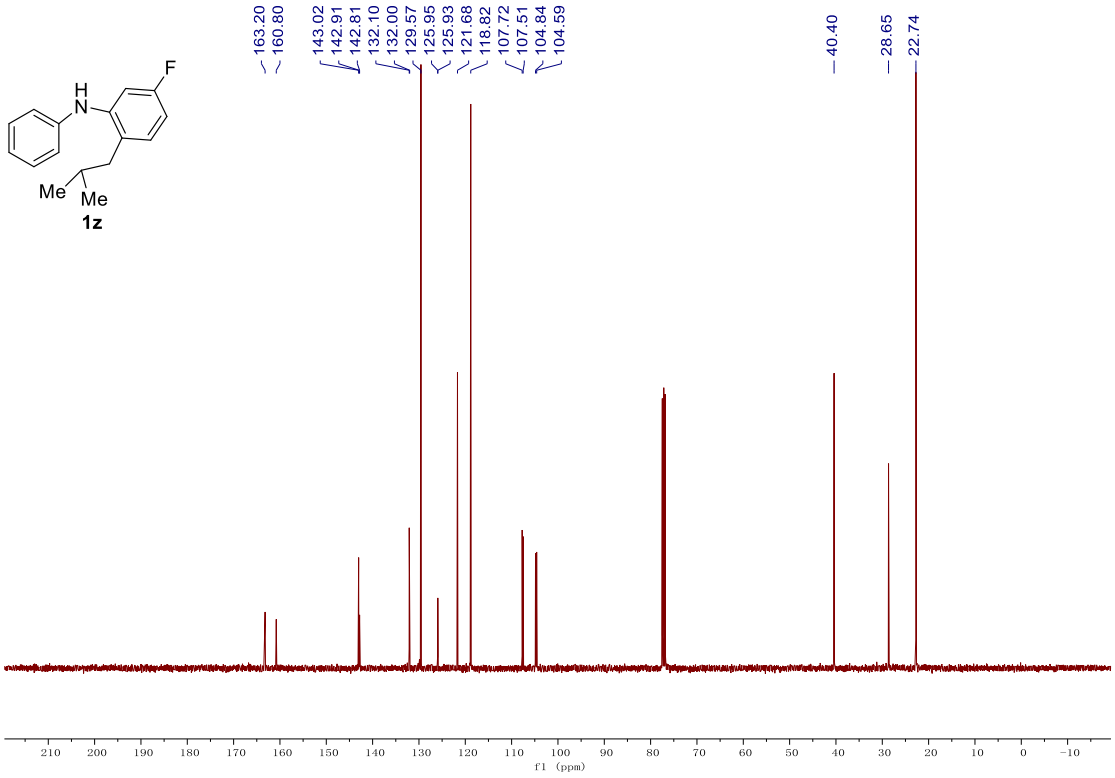
7.32
7.32
7.30
7.10
7.09
7.08
7.07
7.05
7.02
7.00
6.99
6.99
6.98
6.97
6.96
6.65
6.64
6.63
6.62
6.61
6.60
5.52
2.48
2.46
1.99
1.97
1.95
1.93
1.92
1.90
1.88
0.99
0.97
H
N
F
Me
Me
1z
2.00
3.05
2.05
1.00
0.99
2.12
1.15
6.19
f1 (ppm)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132.10
132.00
129.57
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125.93
121.68
118.82
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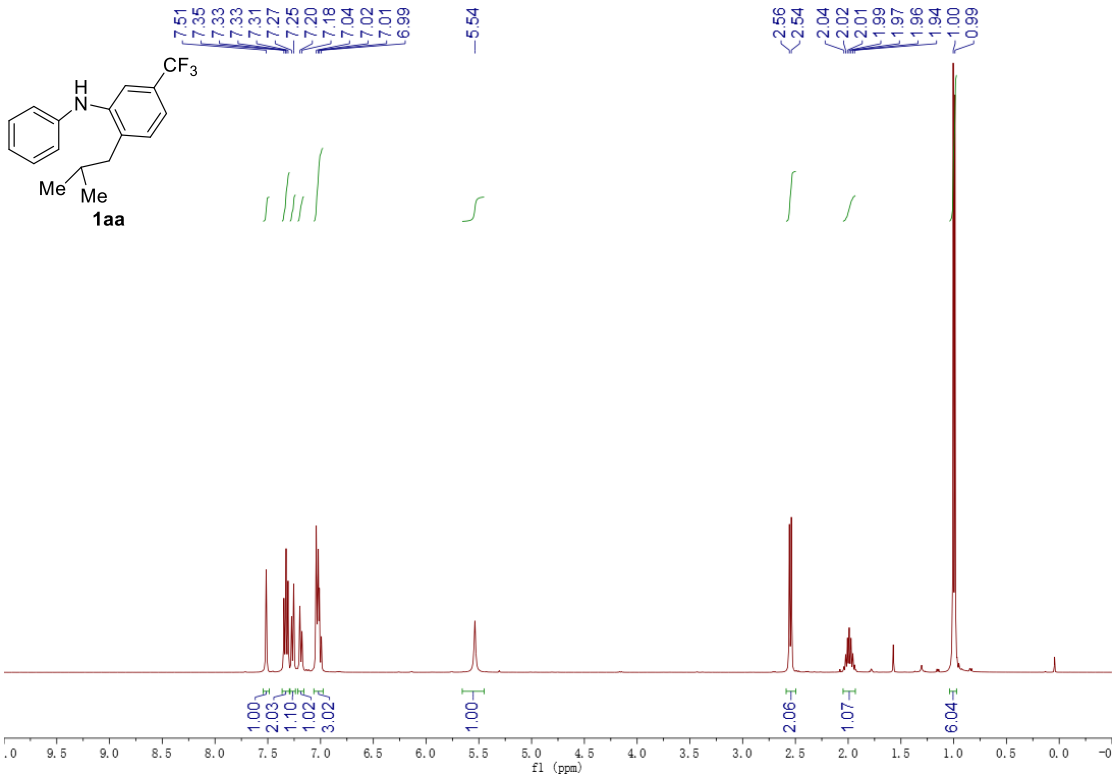
107.51
104.84
104.59
40.40
28.65
22.74
H
N
F
Me
Me
1z
f1 (ppm)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7.33
7.33
7.31
7.27
7.25
7.20
7.18
7.04
7.02
7.01
6.99
5.54
2.56
2.54
2.04
2.02
2.01
1.99
1.97
1.96
1.94
1.00
0.99
CF3
H
N
Me
Me
1aa
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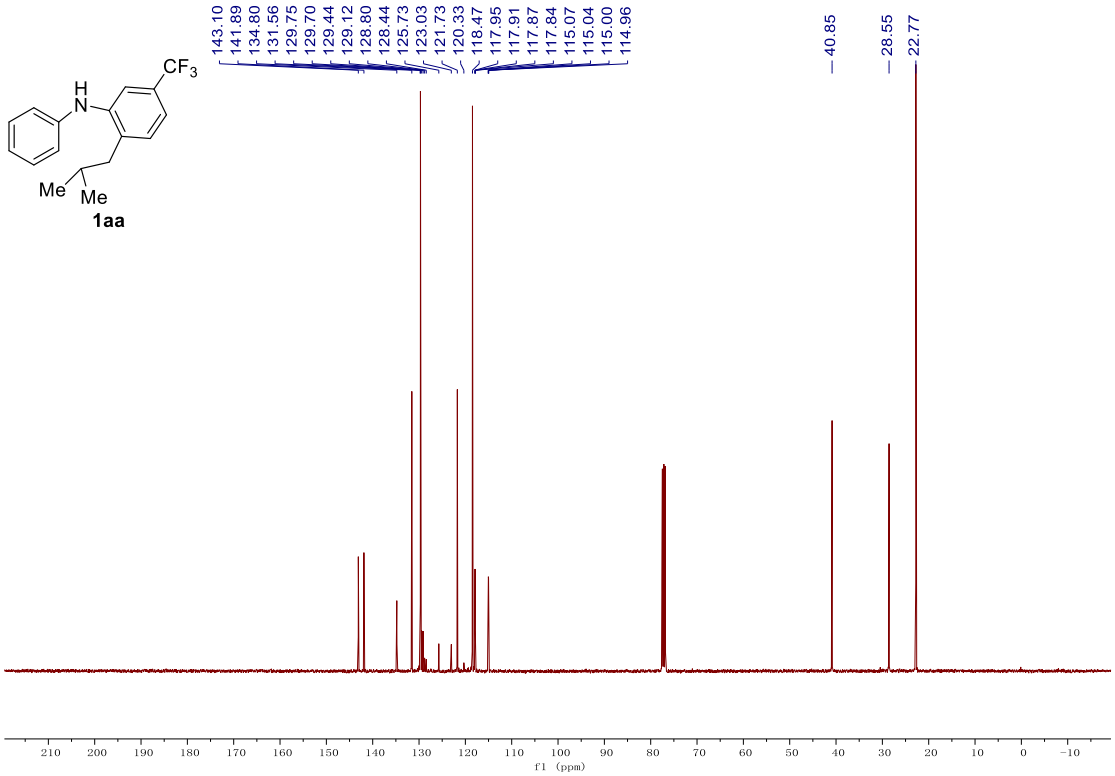
2.03
1.10
1.02
3.02
1.00
2.06
1.07
6.04
f1 (ppm)


143.10
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134.80
131.56
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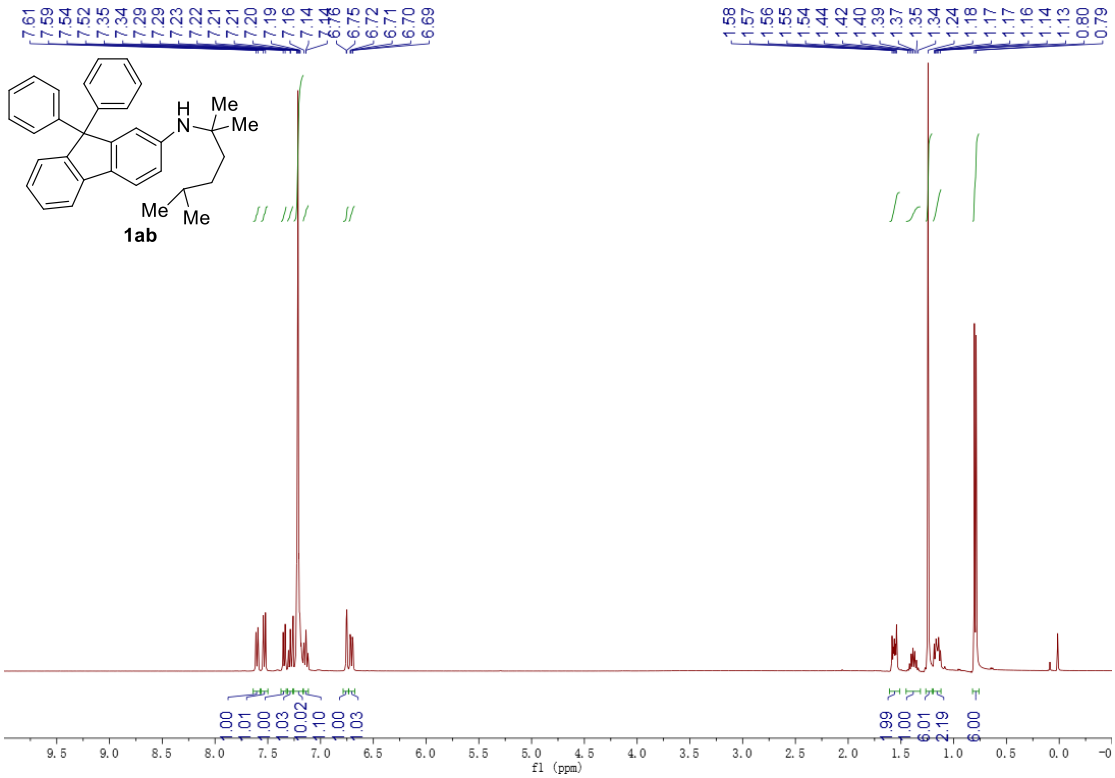
129.70
129.44
129.12
128.80
128.44
125.73
123.03
121.73
120.33
118.47
117.95
117.91
117.87
117.84
115.07
115.04
115.00
114.96
40.85
28.55
22.77
CF3
H
N
Me
Me
1aa
f1 (ppm)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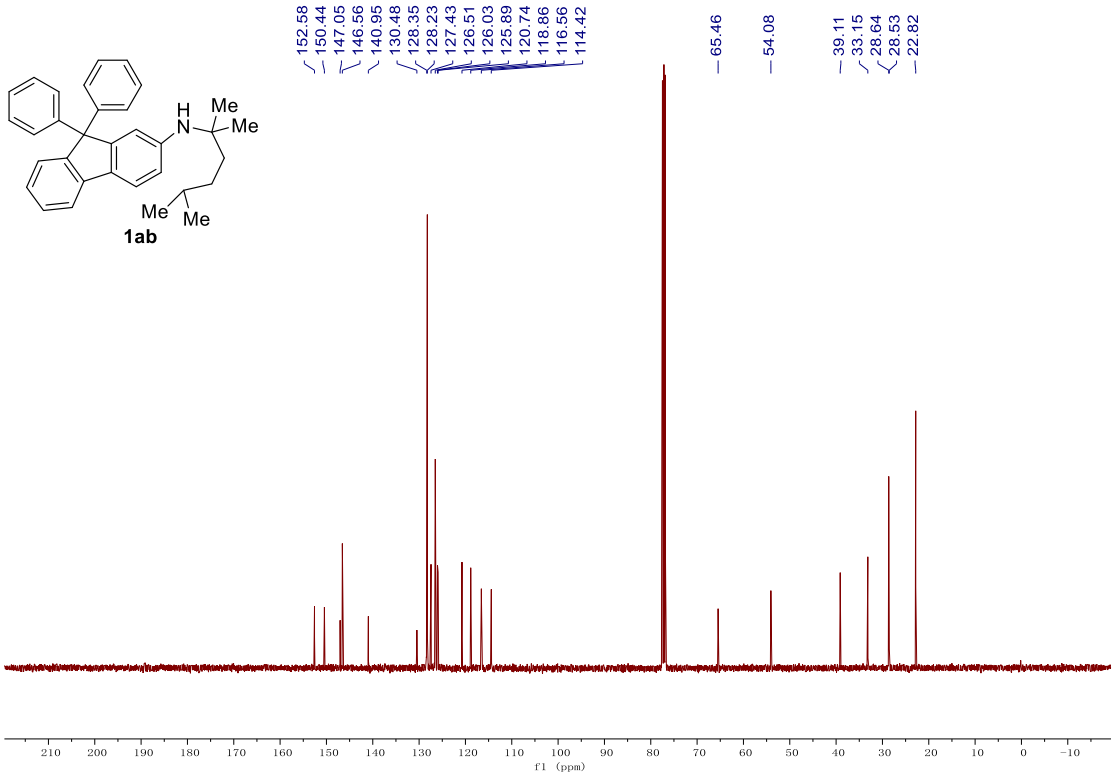
7.59
7.54
7.52
7.35
7.34
7.29
7.29
7.23
7.22
7.21
7.21
7.20
7.19
7.16
7.14
6.75
6.72
6.71
6.70
6.69
1.58
1.57
1.56
1.55
1.54
1.44
1.42
1.40
1.39
1.37
1.35
1.34
1.24
1.18
1.17
1.17
1.16
1.14
1.13
0.80
0.79
H
N
Me
Me
Me
Me
1ab
1.00
1.01
1.00
1.03
10.02
1.10
1.00
1.03
1.99
1.00
6.01
2.19
6.00
f1 (ppm)


152.58
150.44
147.05
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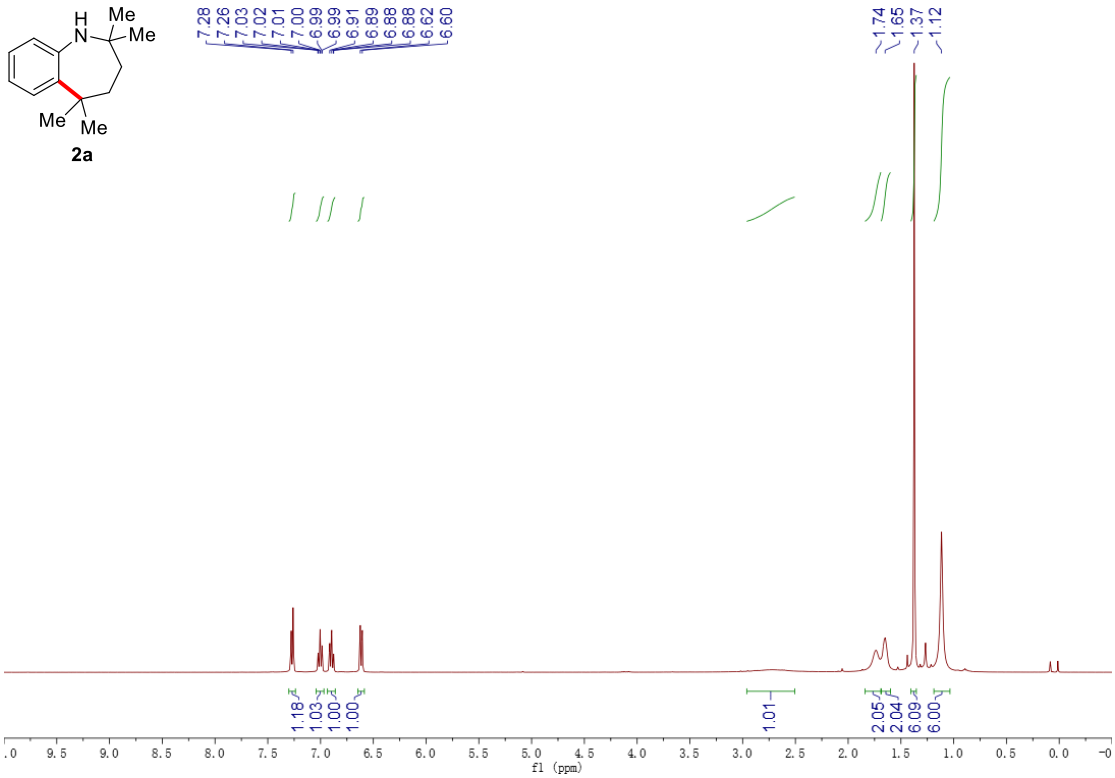
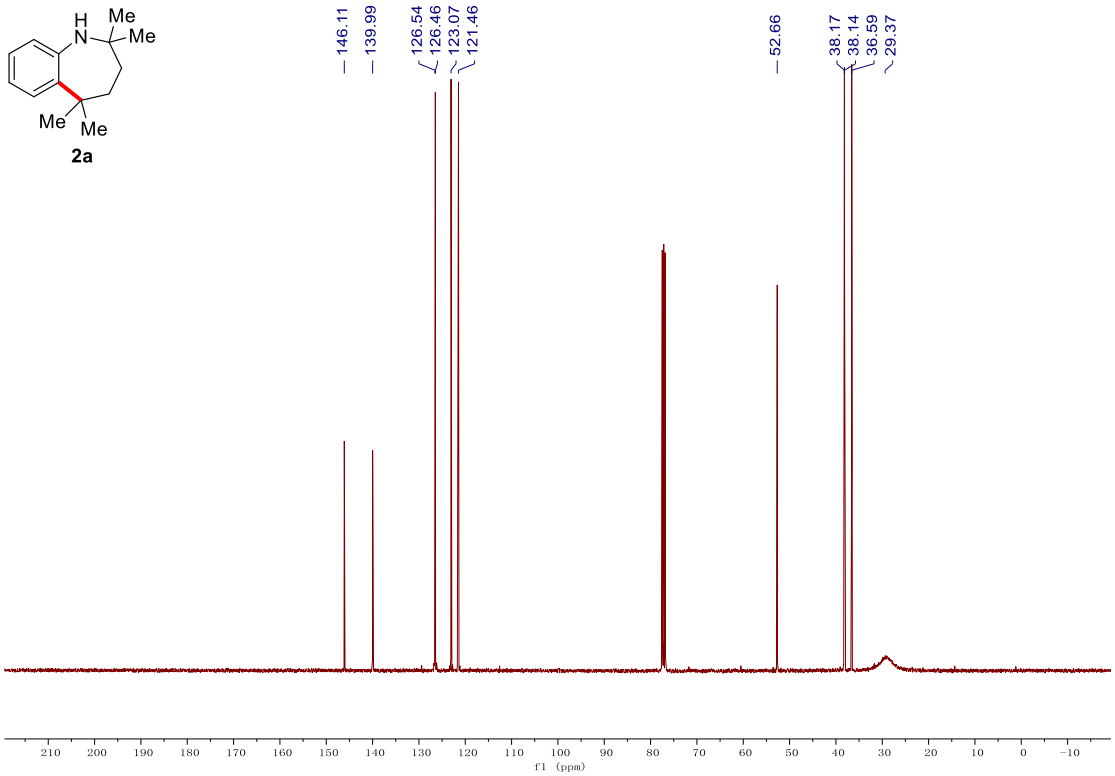
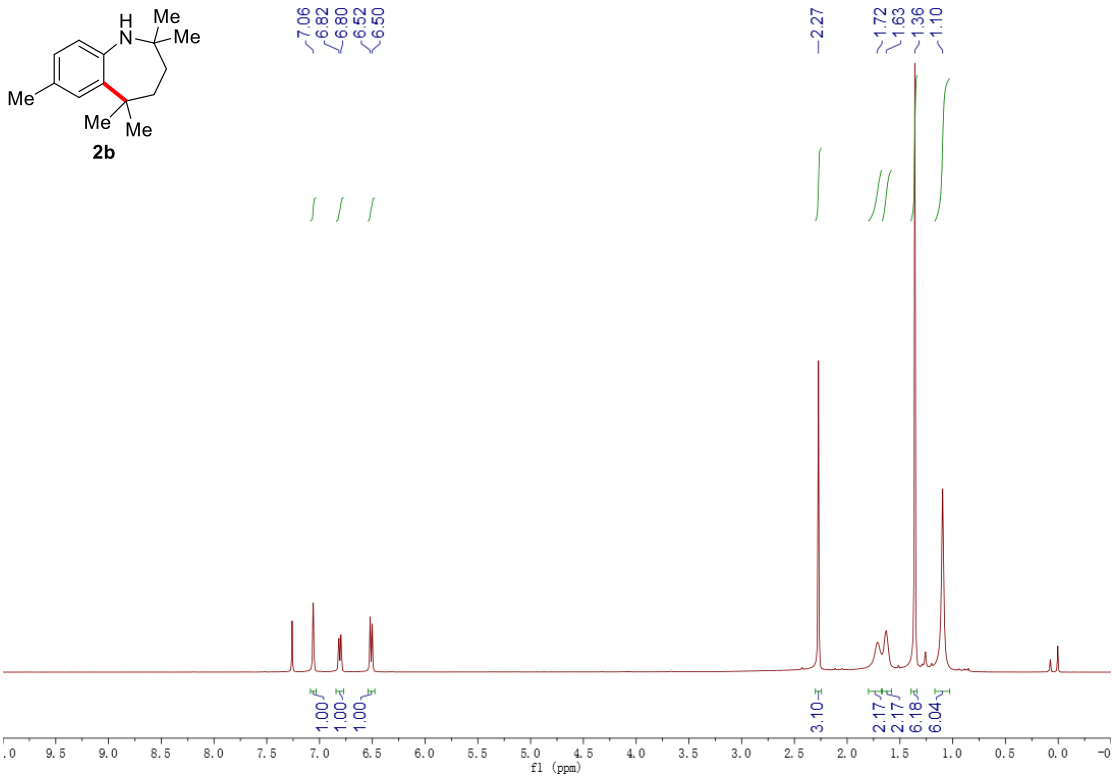
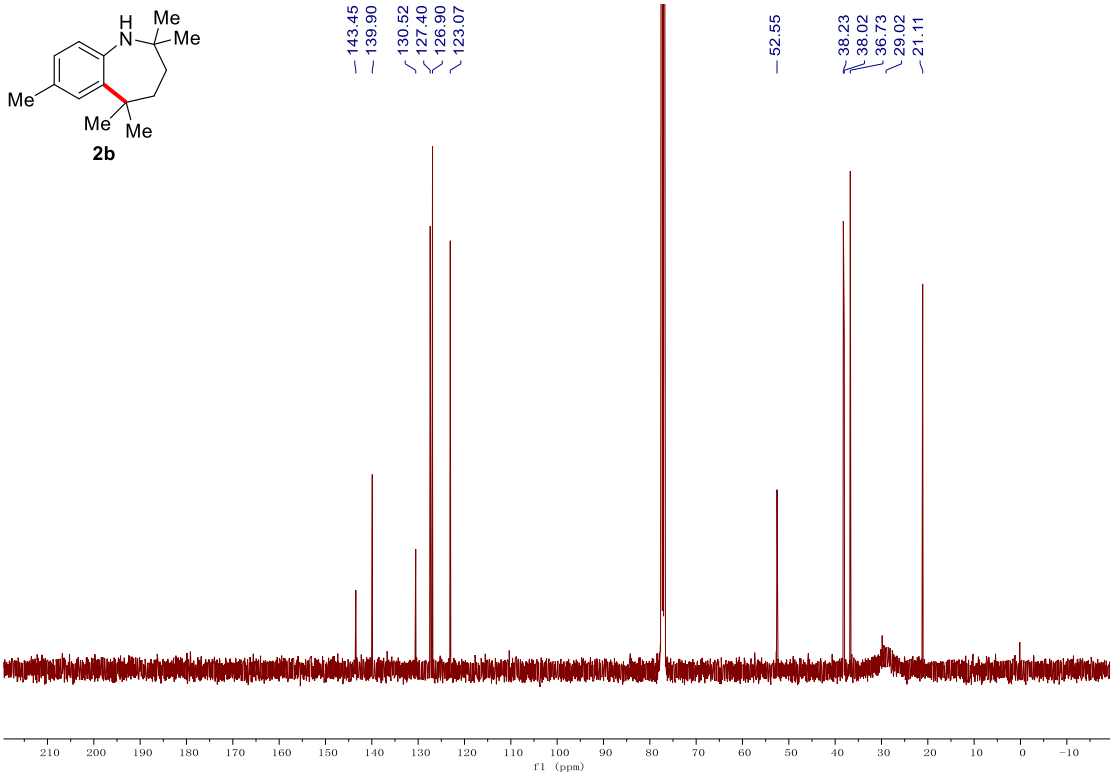
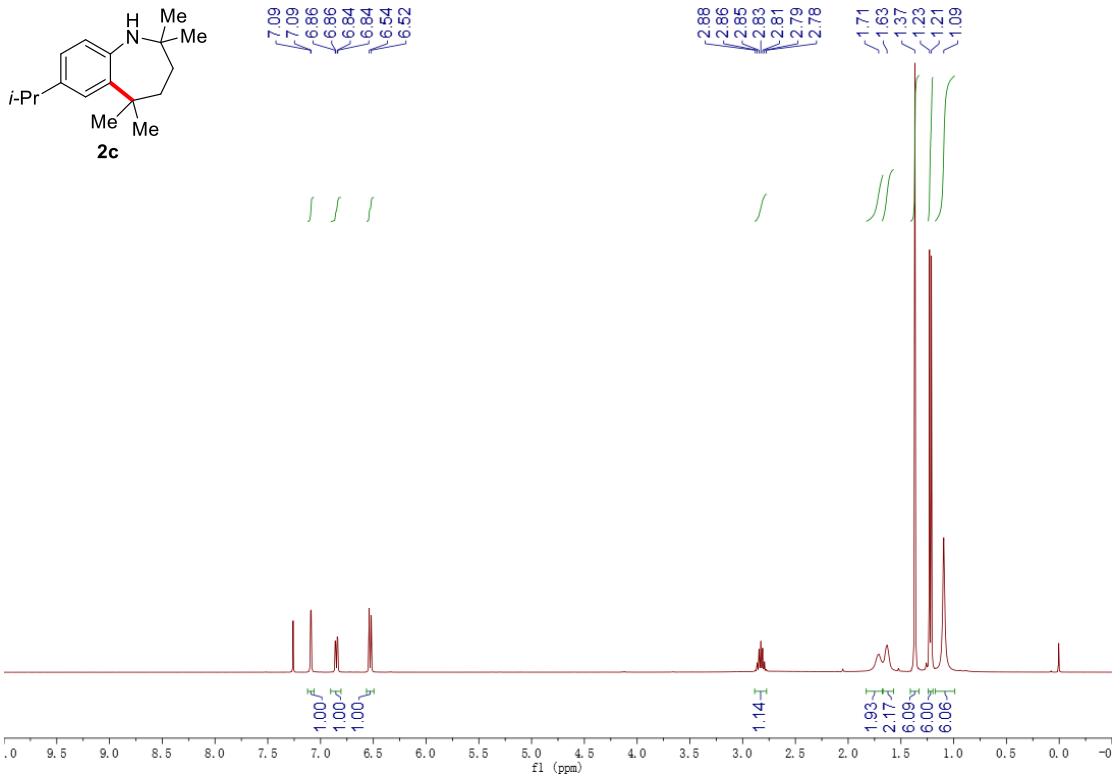
140.95
130.48
128.35
128.23
127.43
126.51
126.03
125.89
120.74
118.86
116.56
114.42
65.46
54.08
39.11
33.15
28.64
28.53
22.82
H
N
Me
Me
Me
Me
1ab
f1 (ppm)

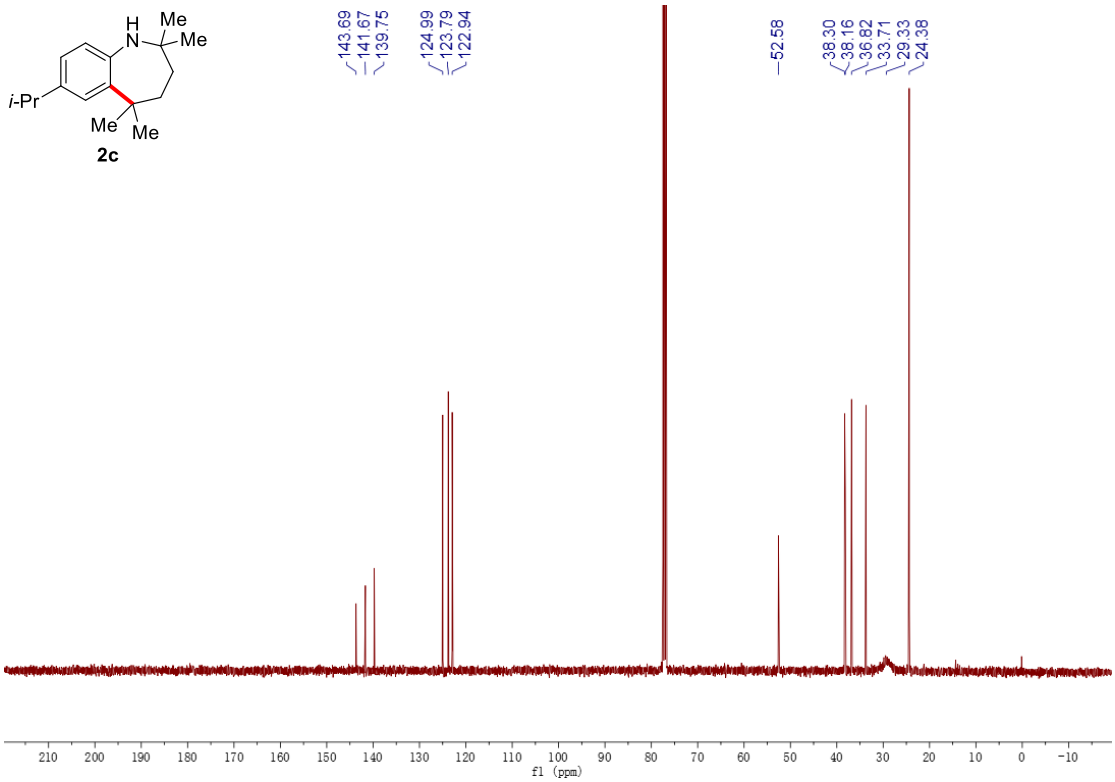

H
N
Me
Me
Me
Me
2a
7.28
7.26
7.03
7.02
7.01
7.00
6.99
6.99
6.91
6.89
6.88
6.88
6.62
6.60
1.74
1.65
1.37
1.12
1.18
1.03
1.00
1.00
1.01
2.05
2.04
6.09
6.00
f1 (ppm)

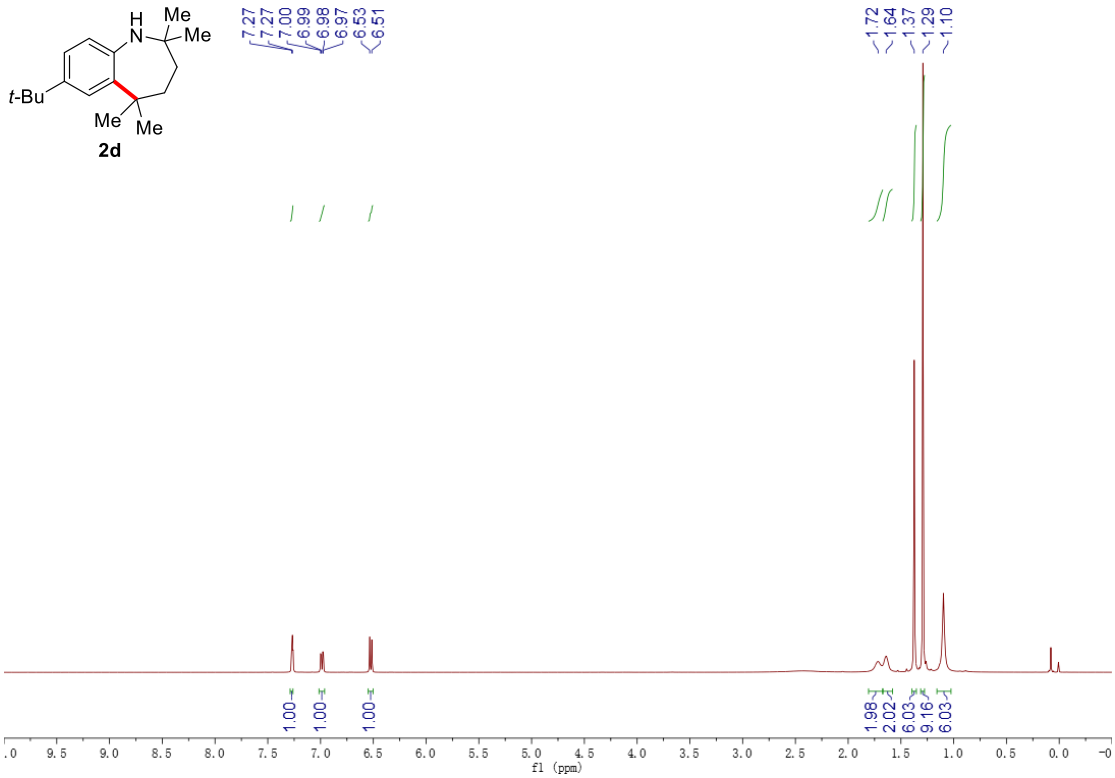

H
N
Me
Me
Me
Me
2a
146.11
139.99
126.54
126.46
123.07
121.46
52.66
38.17
38.14
36.59
29.37
f1 (ppm)

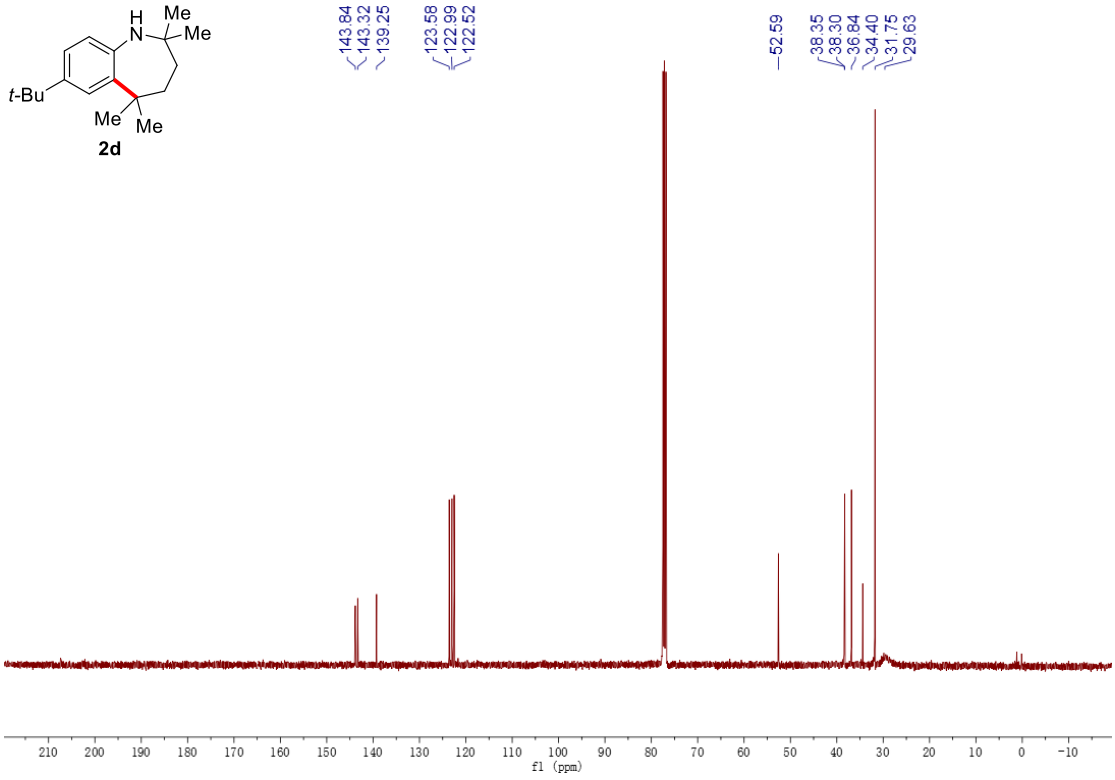

H
N
Me
Me
Me
Me
Me
2b
7.06
6.82
6.80
6.52
6.50
2.27
1.72
1.63
1.36
1.10
1.00
1.00
1.00
3.10
2.17
2.17
6.18
6.04
f1 (ppm)

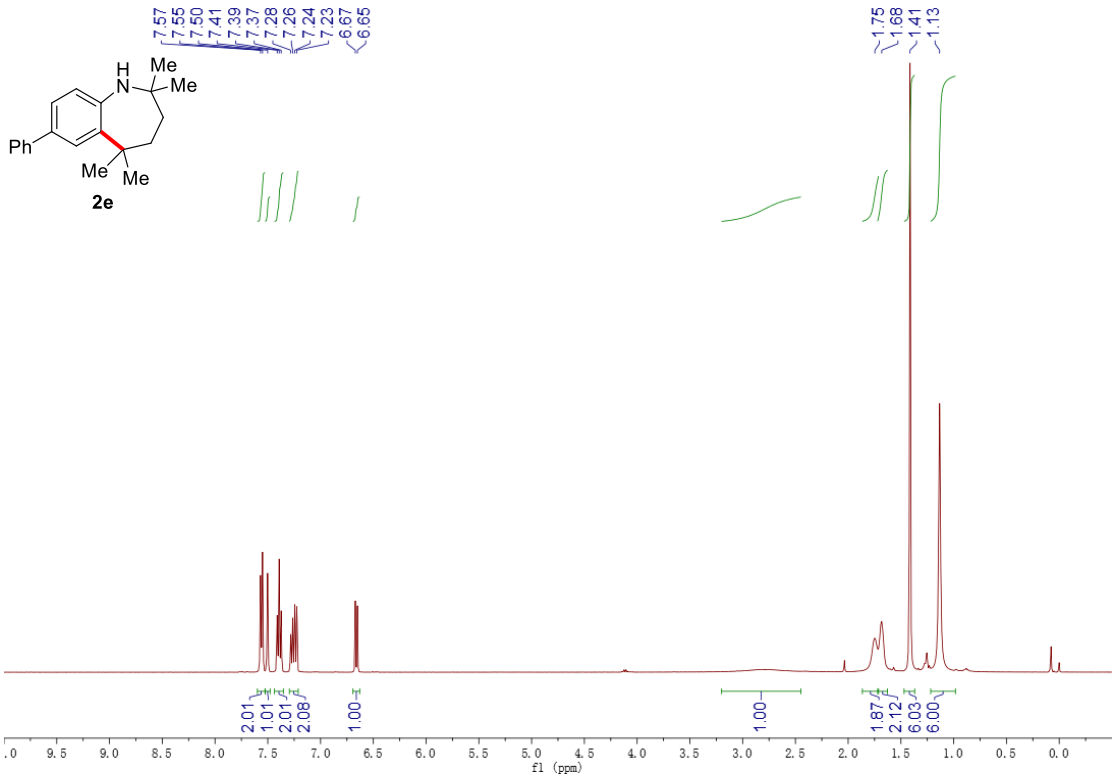

H
N
Me
Me
Me
Me
Me
2b
143.45
139.90
130.52
127.40
126.90
123.07
52.55
38.23
38.02
36.73
29.02
21.11
f1 (ppm)

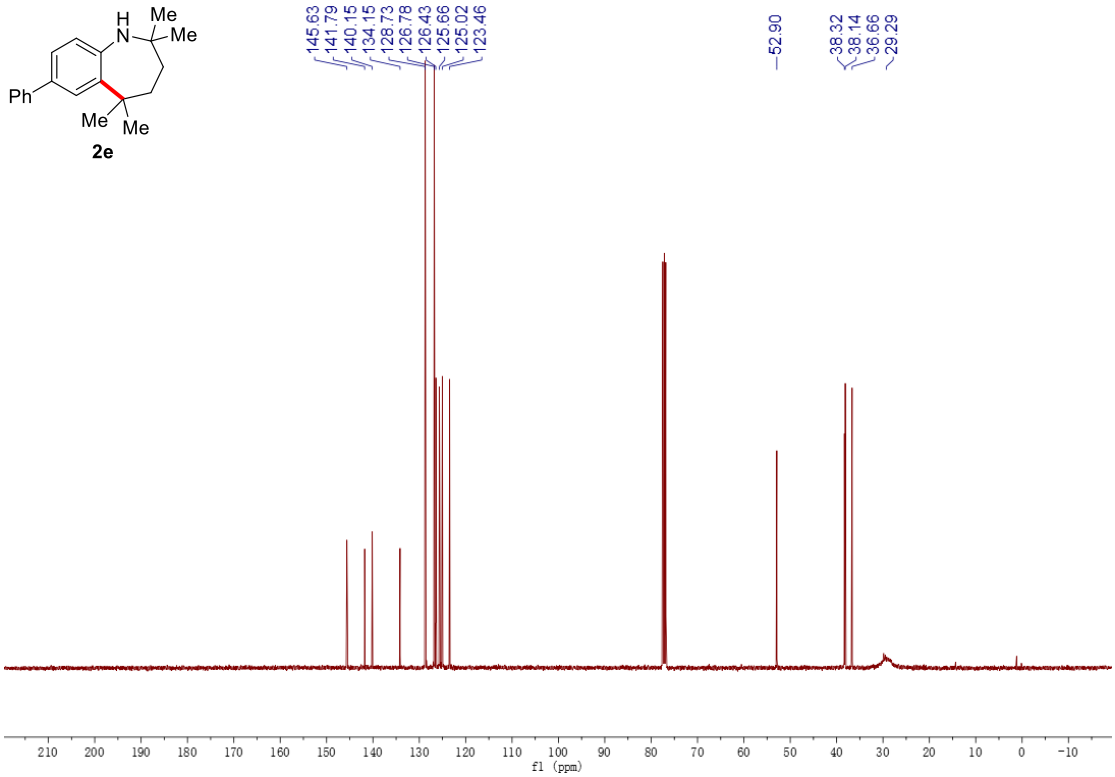

H
N
Me
Me
i-Pr
Me
Me
2c
7.09
7.09
6.86
6.86
6.84
6.84
6.54
6.52
2.88
2.86
2.85
2.83
2.81
2.79
2.78
1.71
1.63
1.37
1.23
1.21
1.09
1.00
1.00
1.00
1.14
1.93
2.17
6.09
6.00
6.06
f1 (ppm)

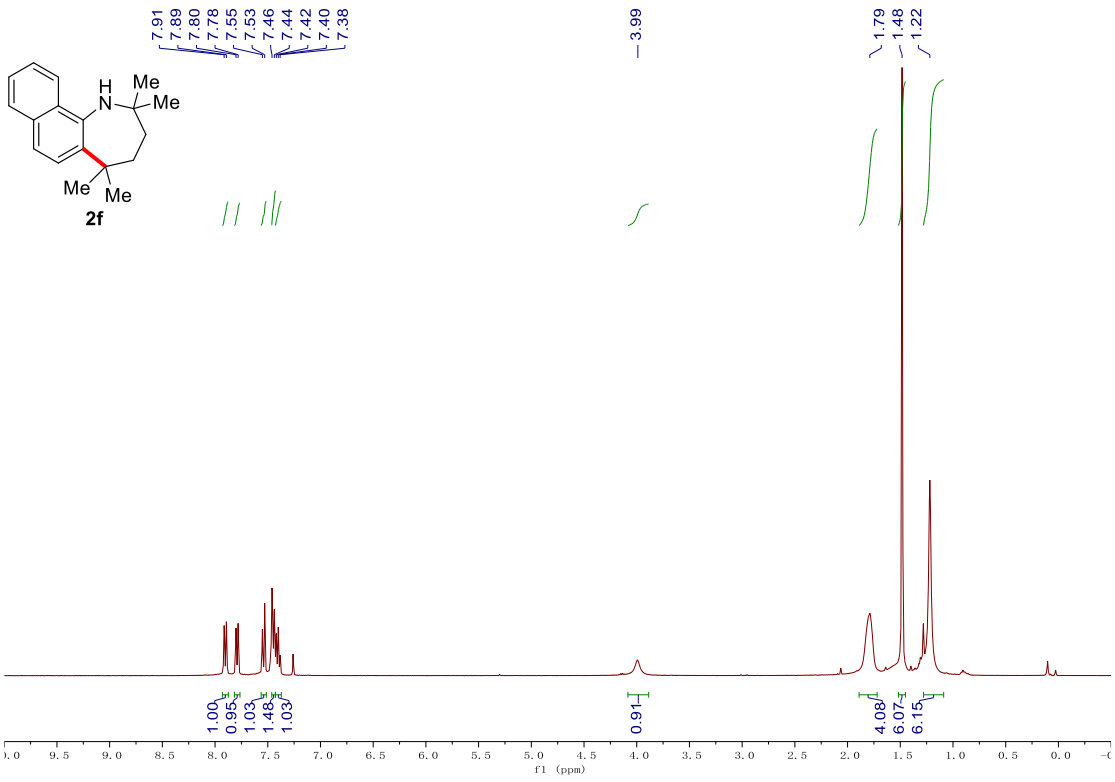

H
N
Me
Me
i-Pr
Me
Me
2c
143.69
141.67
139.75
124.99
123.79
122.94
52.58
38.30
38.16
36.82
33.71
29.33
24.38
f1 (ppm)

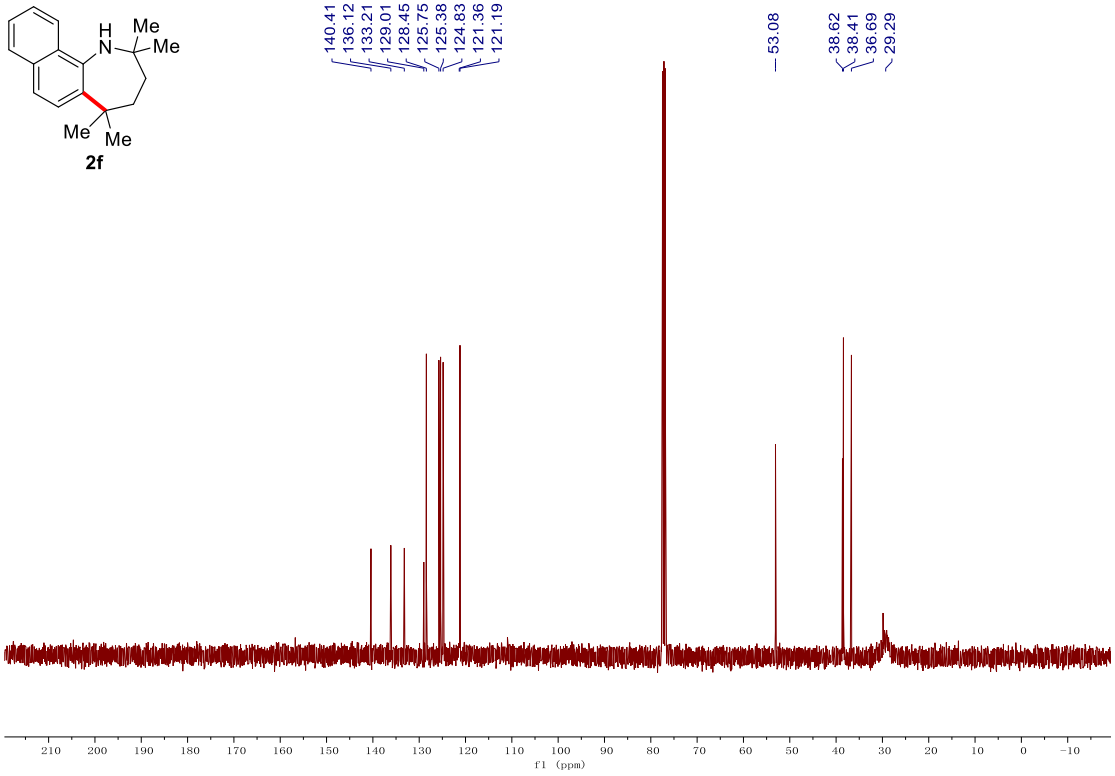

H
N
Me
Me
t-Bu
Me
Me
2d
7.27
7.27
7.00
6.99
6.98
6.97
6.53
6.51
1.72
1.64
1.37
1.29
1.10
1.00
1.00
1.00
1.98
2.02
6.03
9.16
6.03
f1 (ppm)

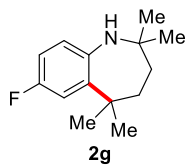

H
N
Me
Me
t-Bu
Me
Me
2d
143.84
143.32
139.25
123.58
122.99
122.52
52.59
38.35
38.30
36.84
34.40
31.75
29.63
f1 (ppm)


7.57
7.55
7.50
7.41
7.39
7.37
7.28
7.26
7.24
7.23
6.67
6.65
1.75
1.68
1.41
1.13
H
N
Me
Me
Ph
Me
Me
2e
2.01
1.01
2.01
2.08
1.00
1.00
1.87
2.12
6.03
6.00
f1 (ppm)


145.63
141.79
140.15
134.15
128.73
126.78
126.43
125.66
125.02
123.46
52.90
38.32
38.14
36.66
29.29
H
N
Me
Me
Ph
Me
Me
2e
f1 (ppm)

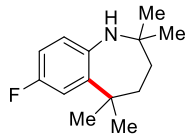

7.91
7.89
7.80
7.78
7.55
7.53
7.46
7.44
7.42
7.40
7.38
3.99
1.79
1.48
1.22
H
N
Me
Me
Me
Me
2f
1.00
0.95
1.03
1.48
1.03
0.91
4.08
6.07
6.15
f1 (ppm)


140.41
136.12
133.21
129.01
128.45
125.75
125.38
124.83
121.36
121.19
53.08
38.62
38.41
36.69
29.29
H
N
Me
Me
Me
Me
2f
f1 (ppm)


H
N
Me
Me
F
Me
Me

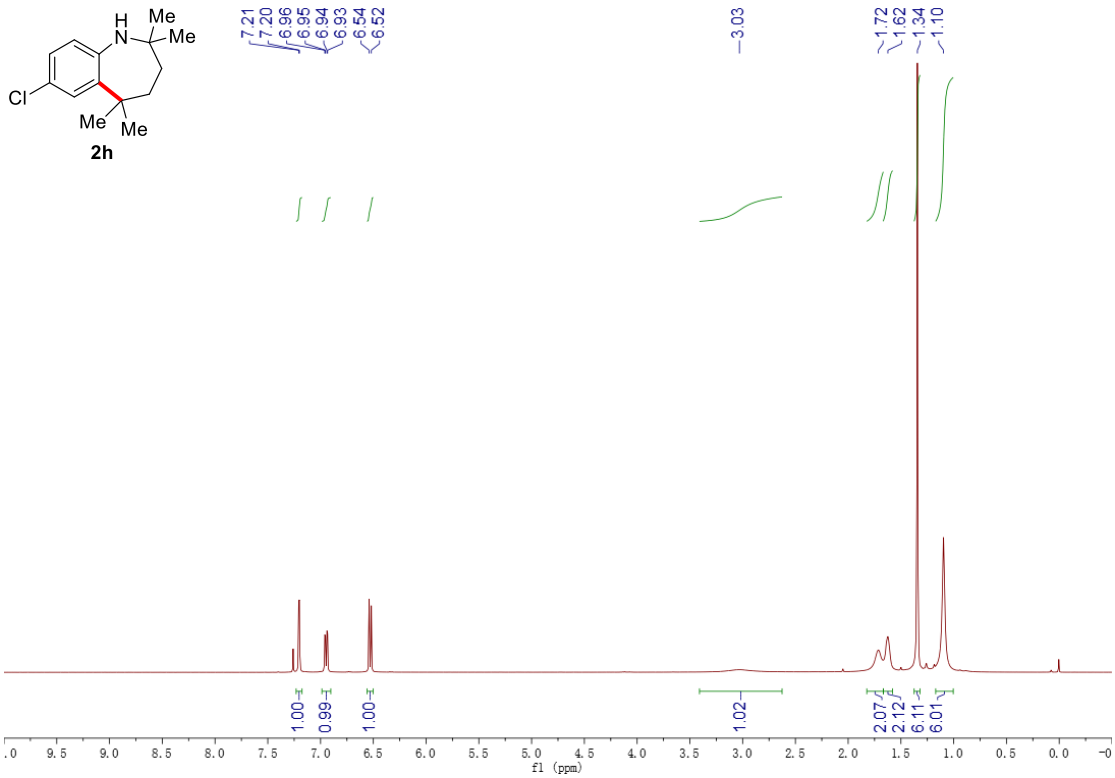
2g

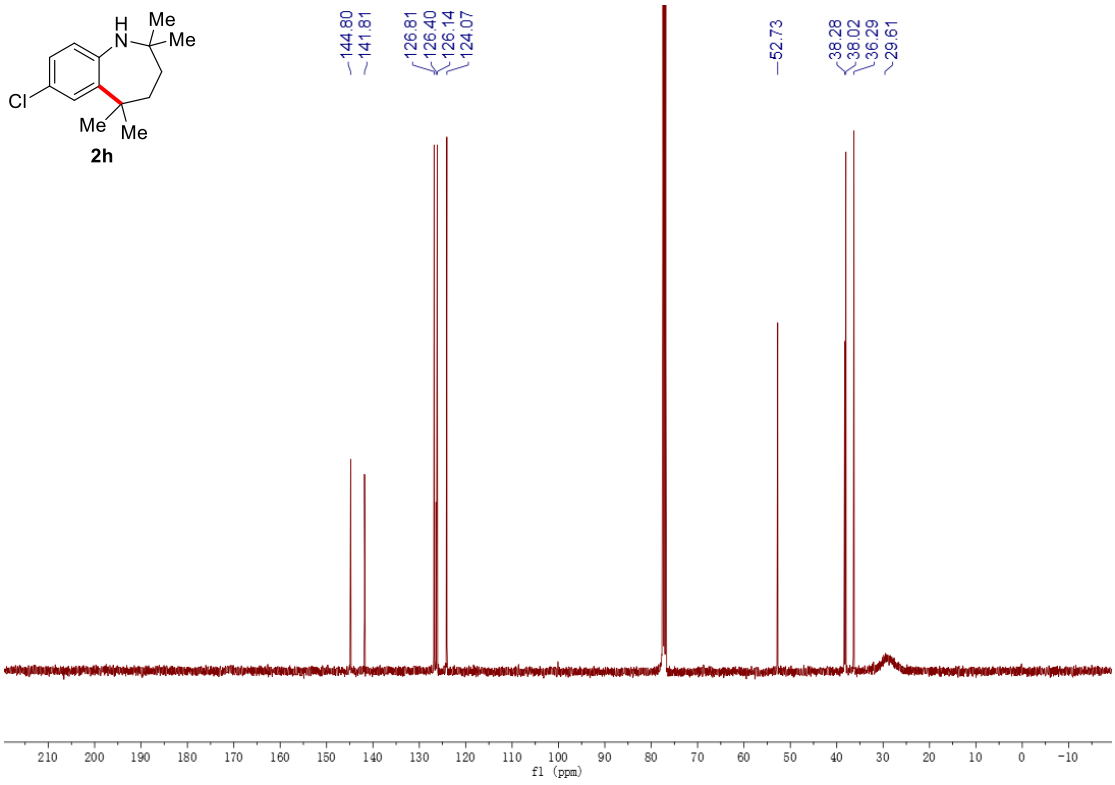
6.98
6.95
6.70
6.68
6.66
6.54
6.53
6.51
1.70
1.62
1.35
1.09
1.00
0.99
1.00
2.11
2.14
6.06
6.04
f1 (ppm)

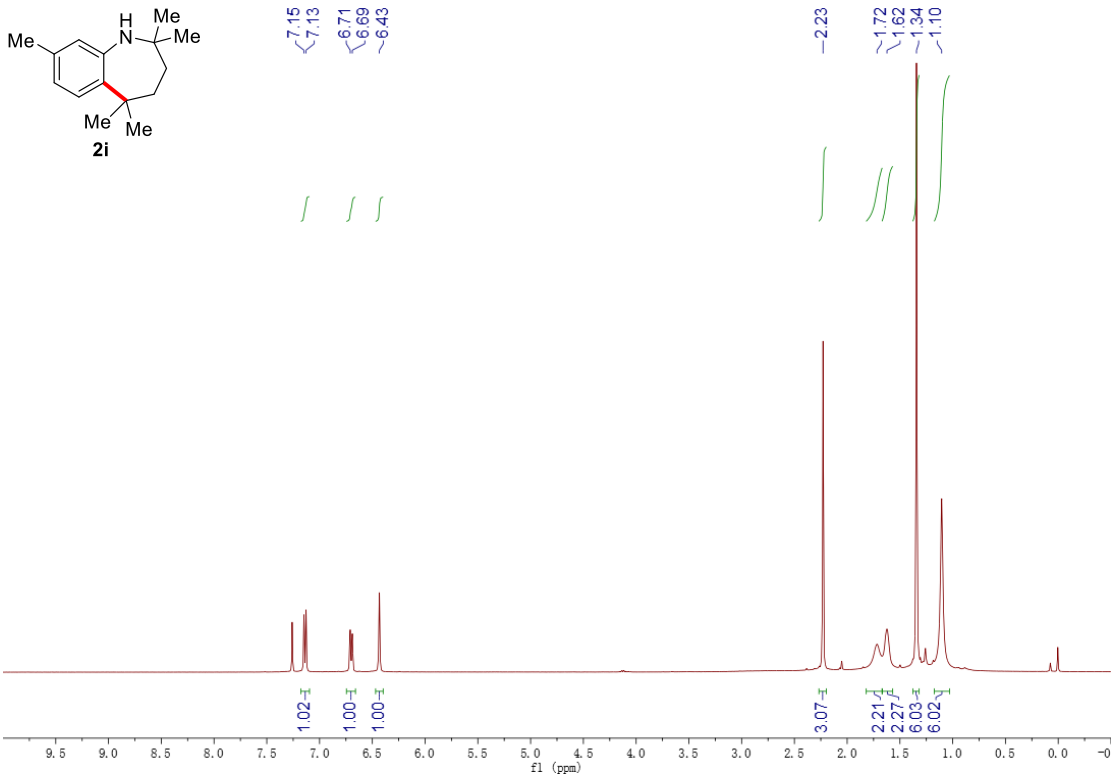

H
N
Me
Me
F
Me
Me

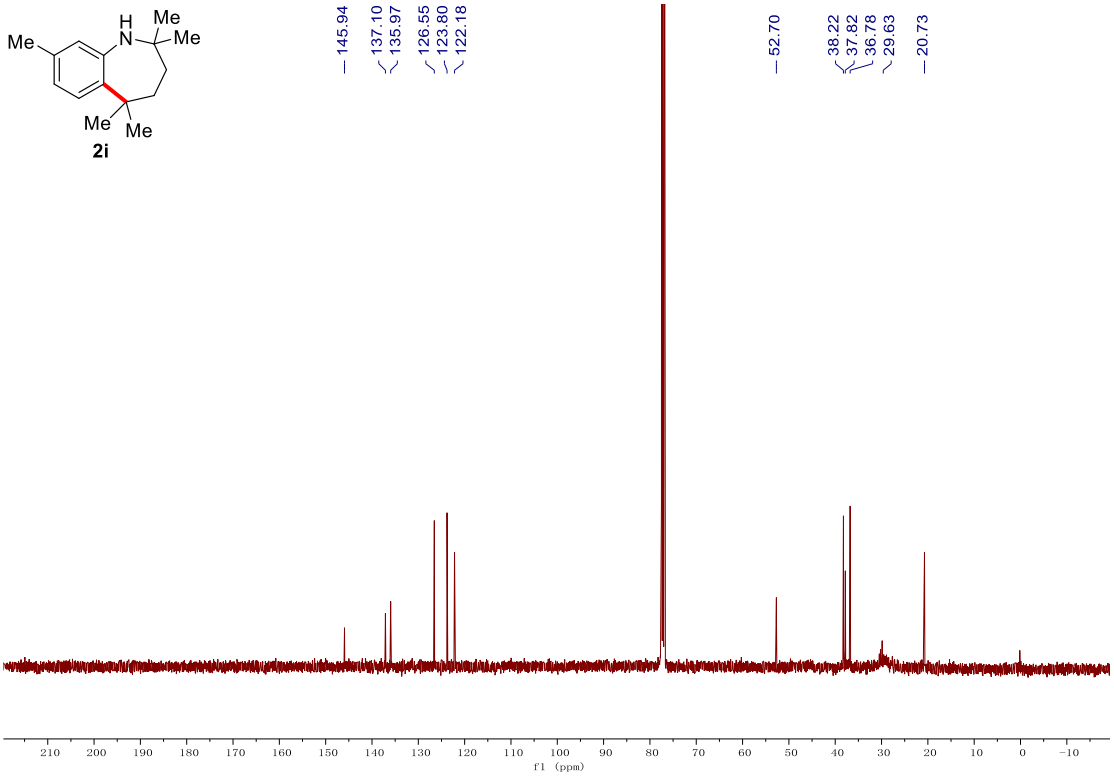
2g

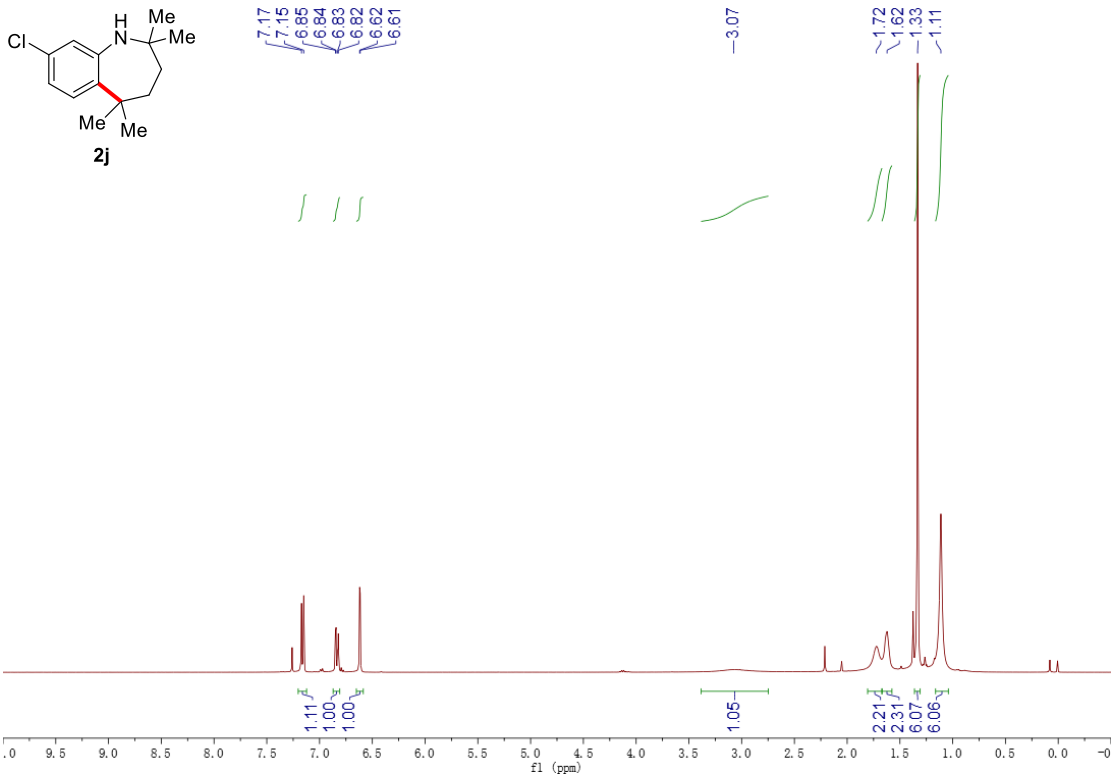
159.53
157.17
142.05
141.99
141.92
141.90
123.57
123.49
113.55
113.32
112.36
112.14
52.36
38.07
36.20
28.70
f1 (ppm)

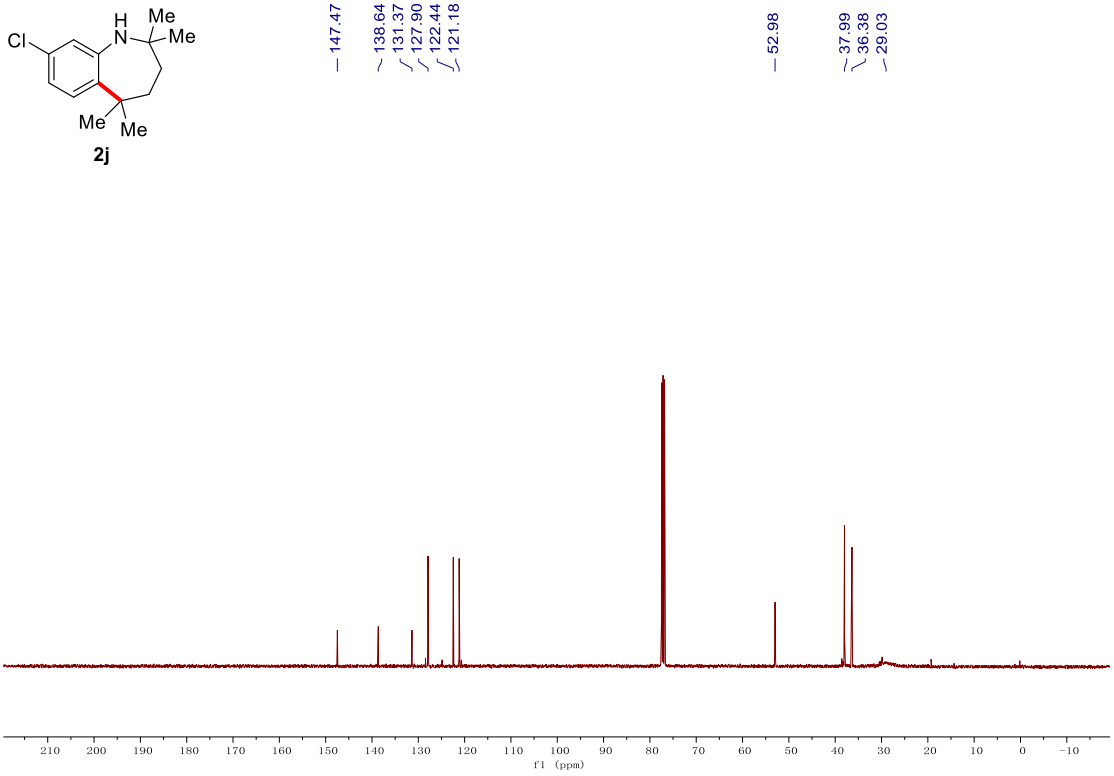

H
N
Me
Me
Cl
Me
Me
2h
7.21
7.20
6.96
6.95
6.94
6.93
6.54
6.52
3.03
1.72
1.62
1.34
1.10
1.00
0.99
1.00
1.02
2.07
2.12
6.11
6.01
f1 (ppm)

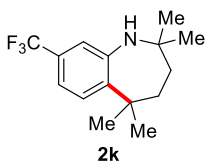

H
N
Me
Me
Cl
Me
Me
2h
144.80
141.81
126.81
126.40
126.14
124.07
52.73
38.28
38.02
36.29
29.61
f1 (ppm)


Me
H
N
Me
Me
Me
Me
2i
7.15
7.13
6.71
6.69
6.43
2.23
1.72
1.62
1.34
1.10
1.02
1.00
1.00
3.07
2.21
2.27
6.03
6.02
f1 (ppm)


Me
H
N
Me
Me
Me
Me
2i
145.94
137.10
135.97
126.55
123.80
122.18
52.70
38.22
37.82
36.78
29.63
20.73
f1 (ppm)

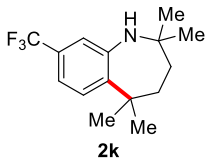

Cl
H
N
Me
Me
Me
Me
2j
7.17
7.15
6.85
6.84
6.83
6.82
6.62
6.61
3.07
1.72
1.62
1.33
1.11
1.11
1.00
1.00
1.05
2.21
2.31
6.07
6.06
f1 (ppm)


Cl
H
N
Me
Me
Me
Me
2j
147.47
138.64
131.37
127.90
122.44
121.18
52.98
37.99
36.38
29.03
f1 (ppm)


F3C
H
N
Me
Me
Me
Me

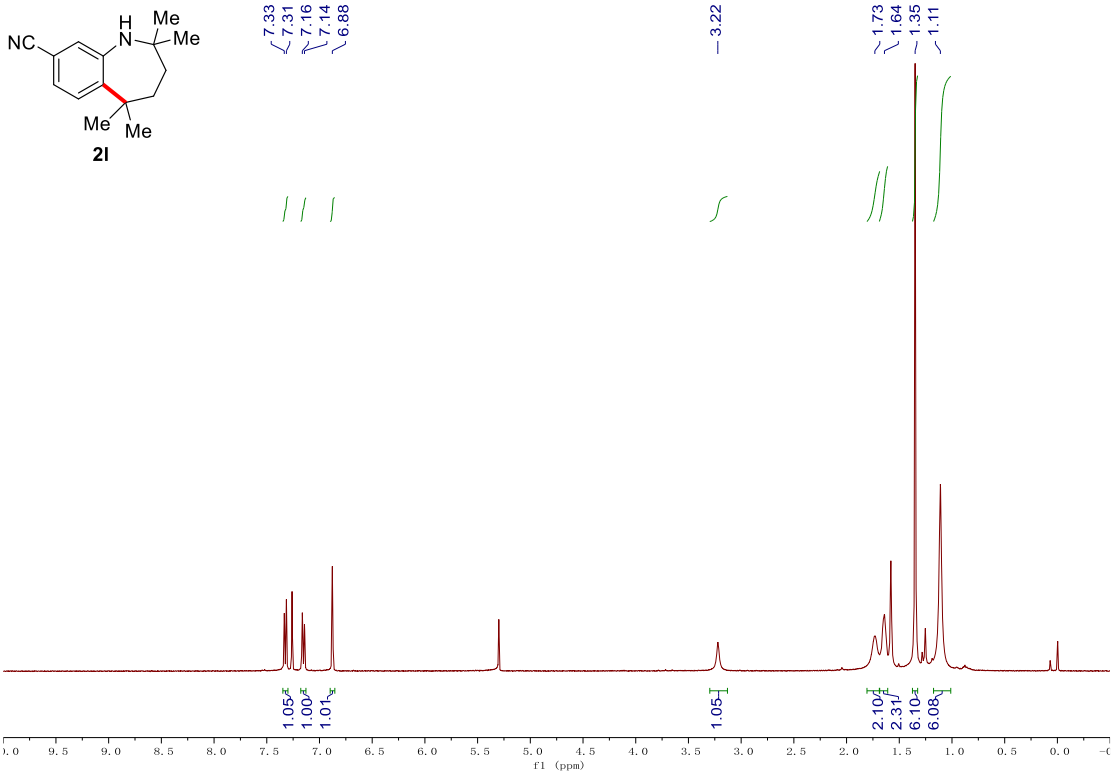
2k

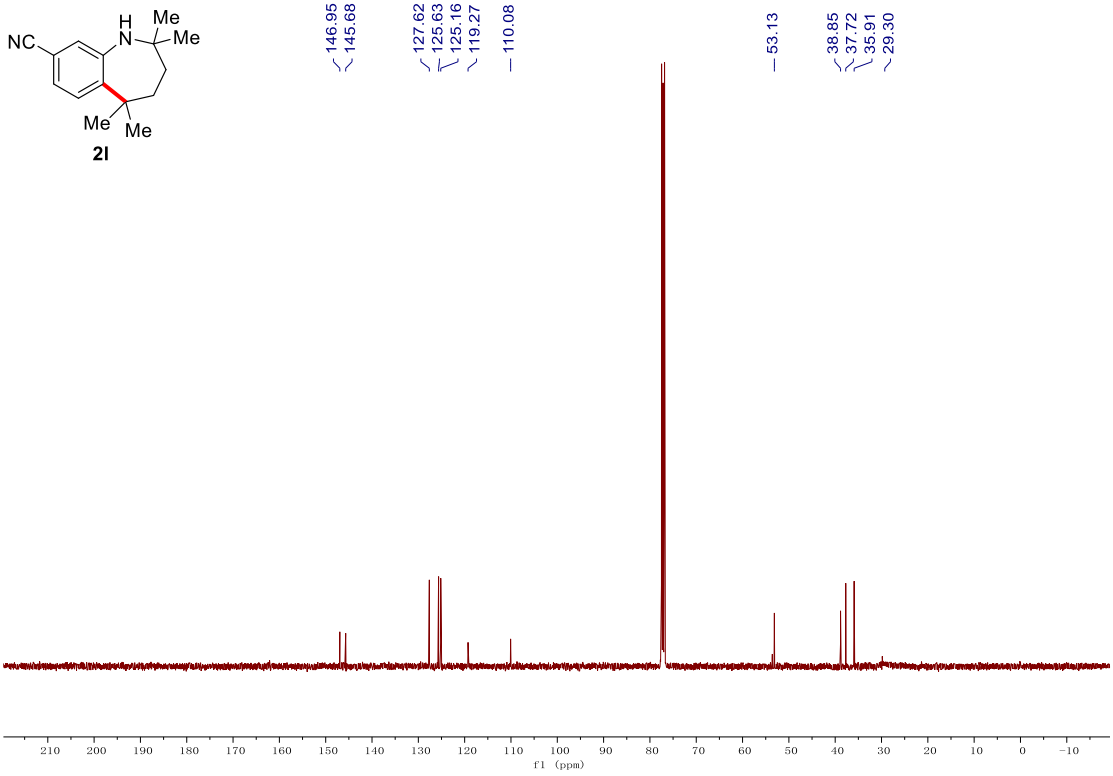
7.36
7.34
7.12
7.12
7.10
6.84
6.84
3.23
1.74
1.65
1.37
1.12
1.02
1.00
1.00
1.01
2.05
2.05
6.06
6.00
f1 (ppm)

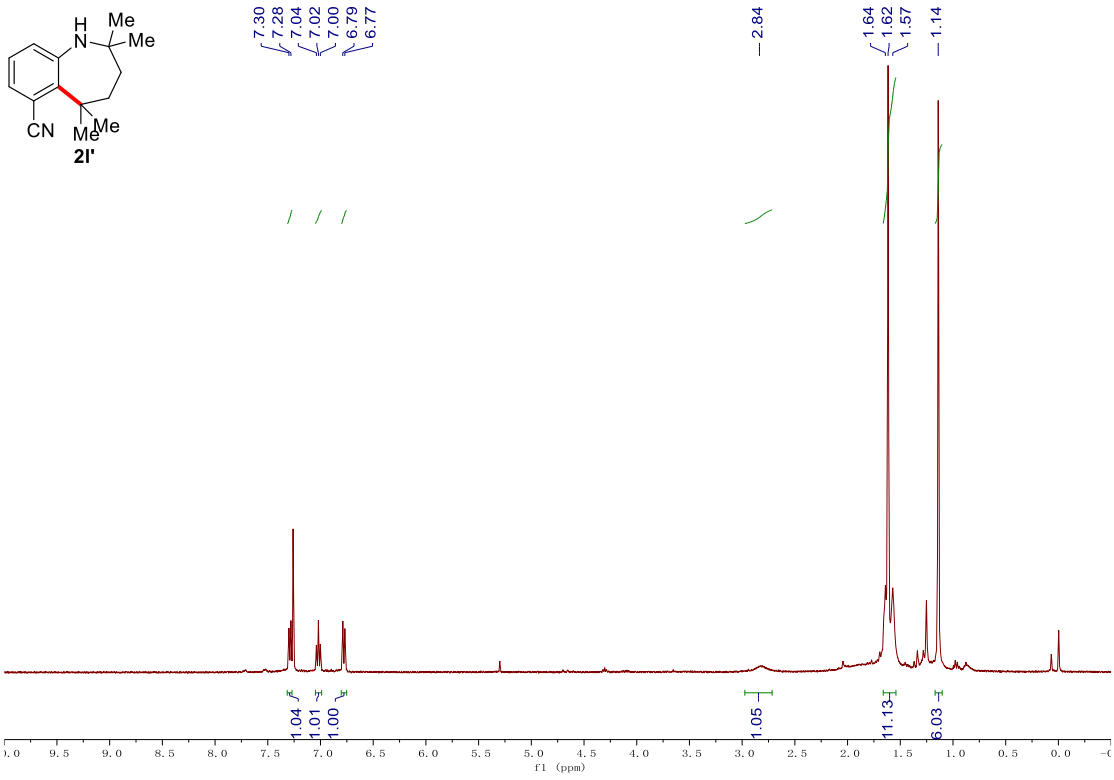

F3C
H
N
Me
Me
Me
Me

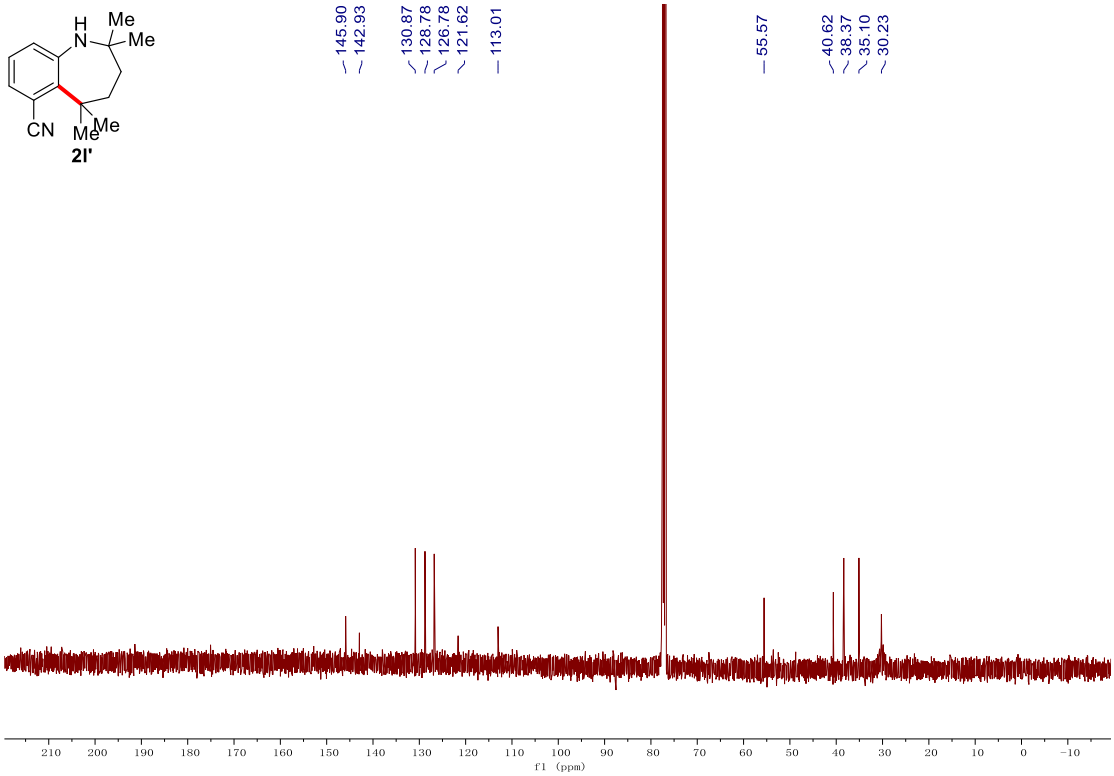
2k

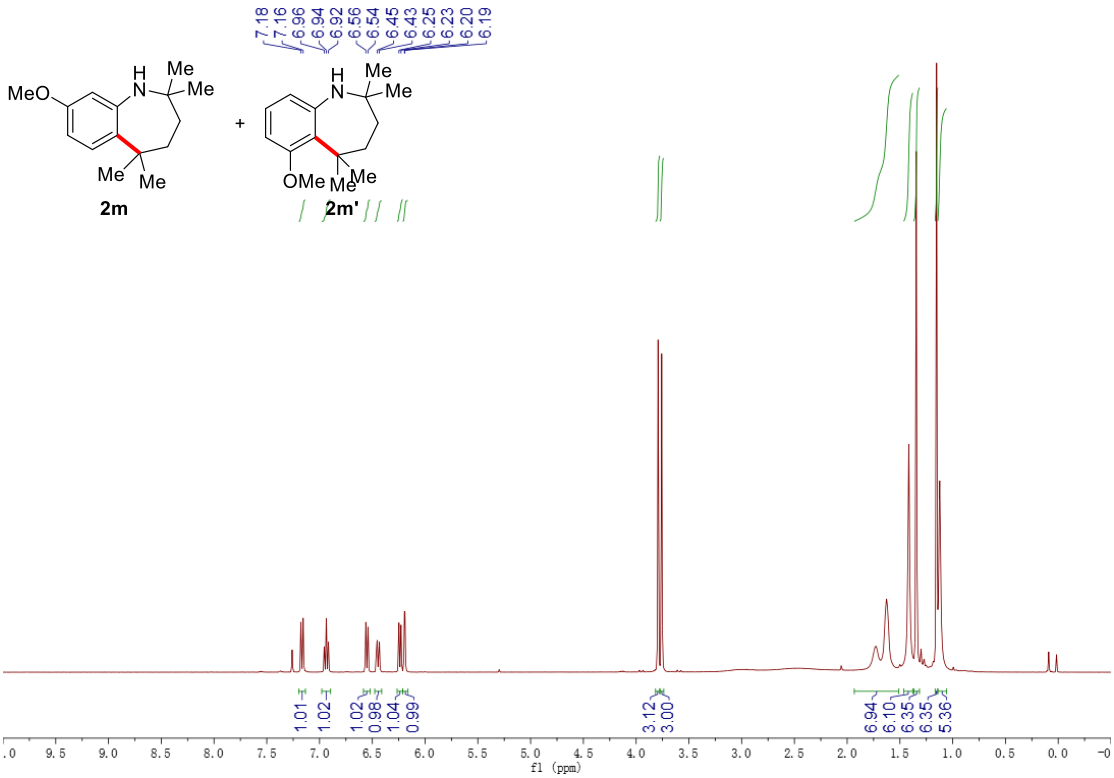
146.56
143.77
129.17
128.85
128.53
128.43
128.21
127.15
125.73
123.03
120.33
119.28
119.25
119.21
119.18
118.07
118.03
117.99
117.95
52.98
38.47
37.90
36.12
29.87
f1 (ppm)

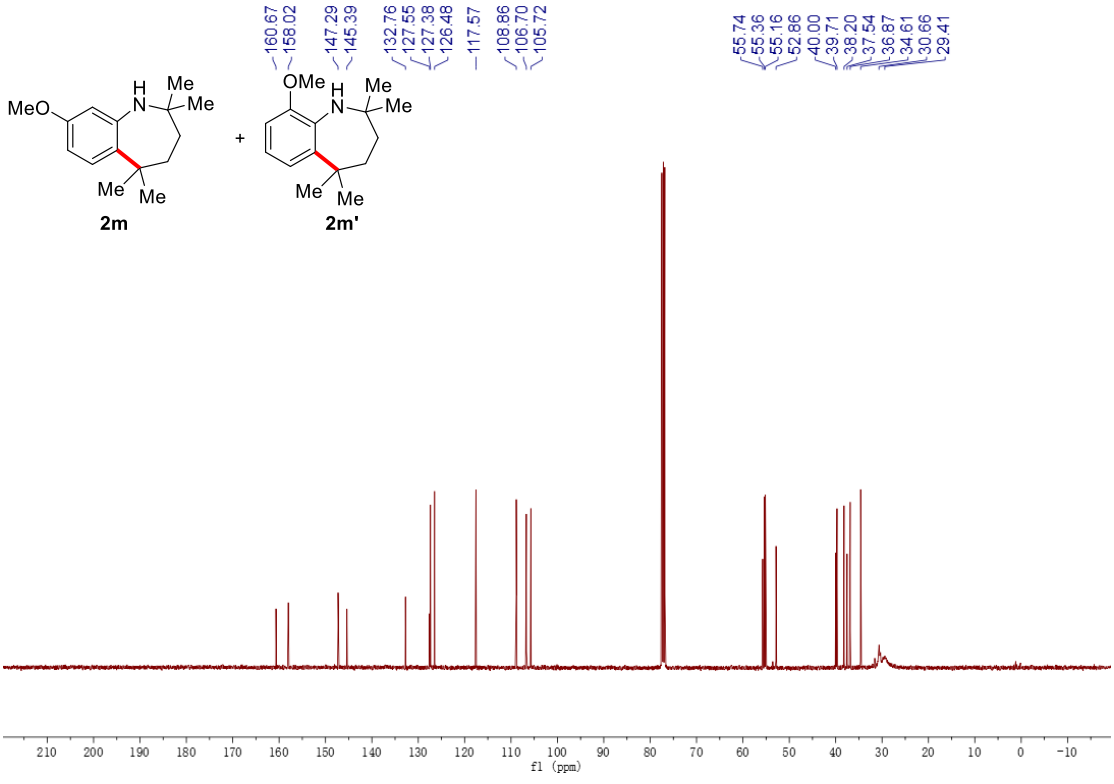

NC
H
N
Me
Me
Me
Me
2l
7.33
7.31
7.16
7.14
6.88
3.22
1.73
1.64
1.35
1.11
1.05
1.00
1.01
1.05
2.10
2.31
6.10
6.08
f1 (ppm)

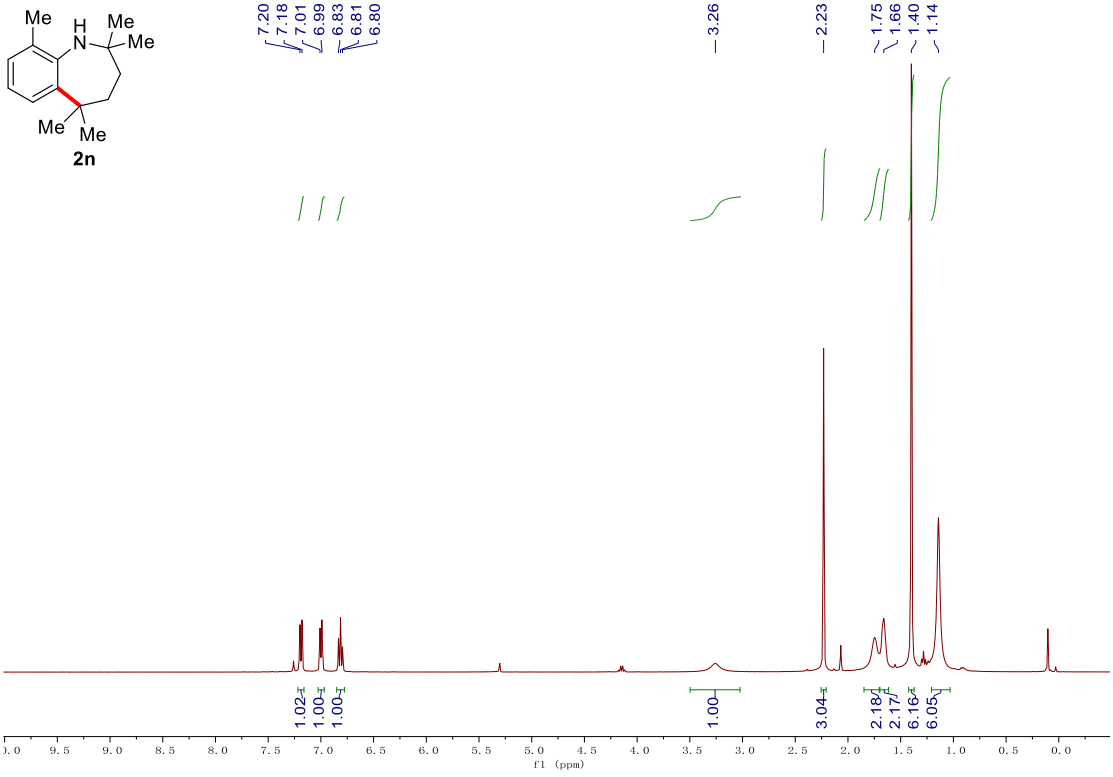

NC
H
N
Me
Me
Me
Me
2l
146.95
145.68
127.62
125.63
125.16
119.27
110.08
53.13
38.85
37.72
35.91
29.30
f1 (ppm)

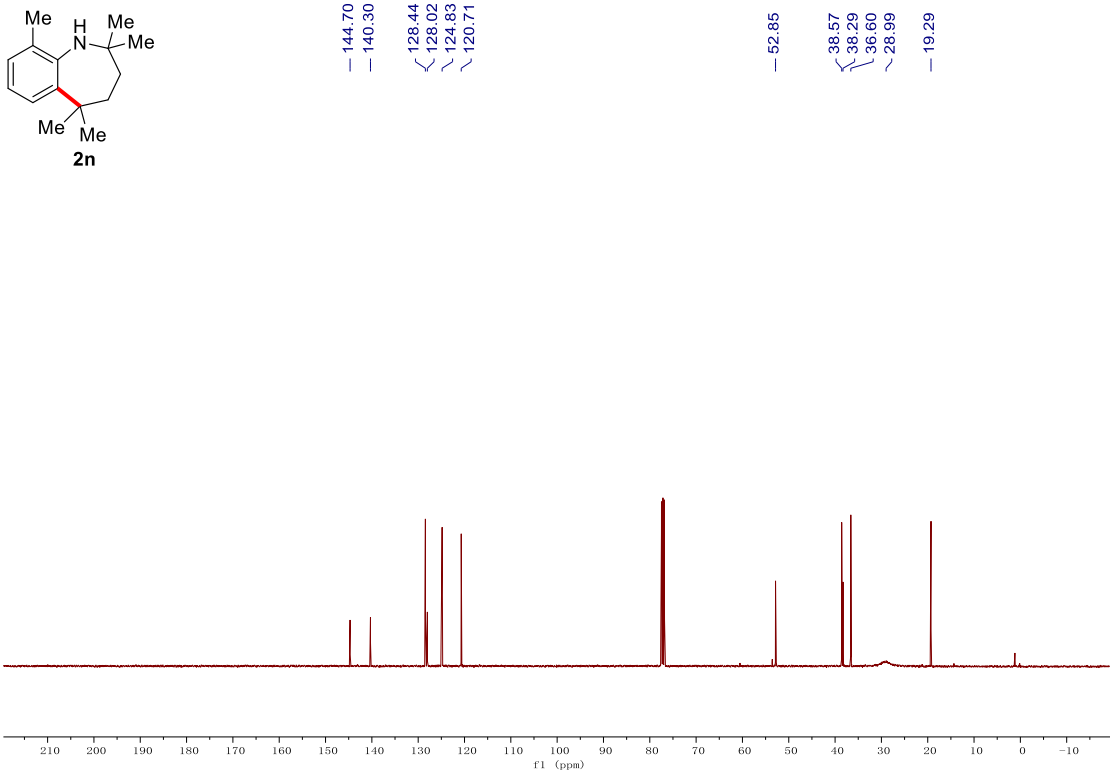

H
N
Me
Me
CN
Me
Me
2l'
7.30
7.28
7.04
7.02
7.00
6.79
6.77
2.84
1.64
1.62
1.57
1.14
1.04
1.01
1.00
1.05
11.13
6.03
f1 (ppm)

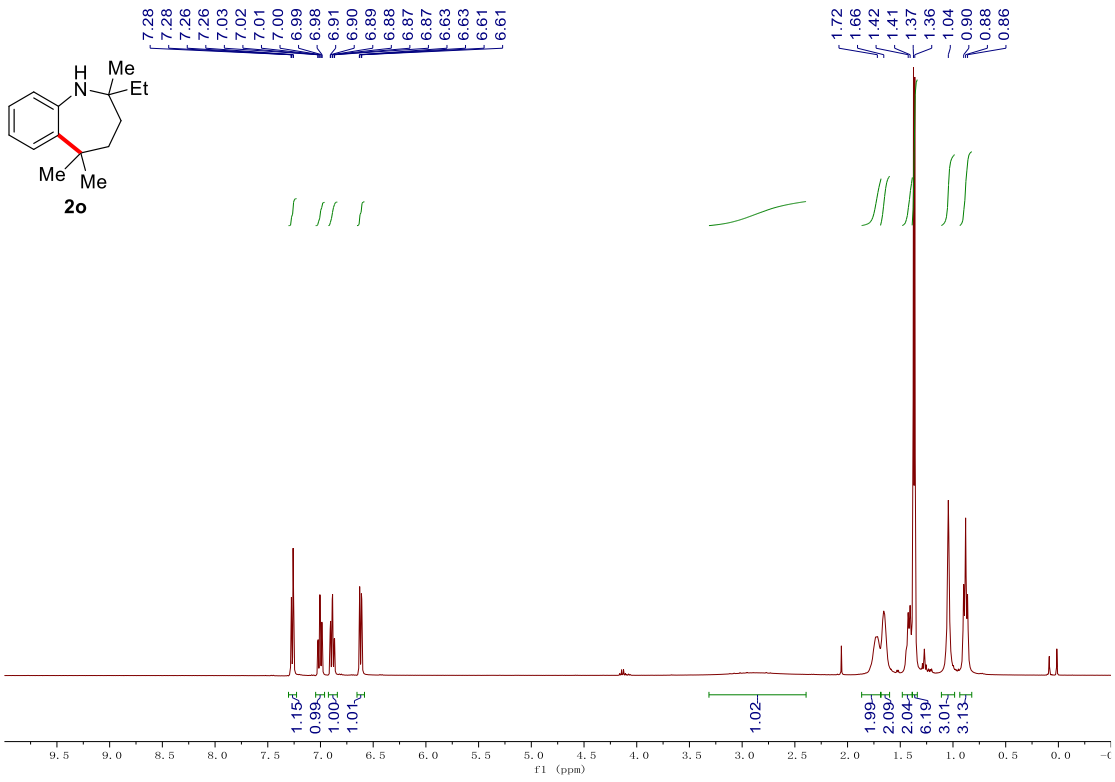

H
N
Me
Me
CN
Me
Me
2l'
145.90
142.93
130.87
128.78
126.78
121.62
113.01
55.57
40.62
38.37
35.10
30.23
f1 (ppm)

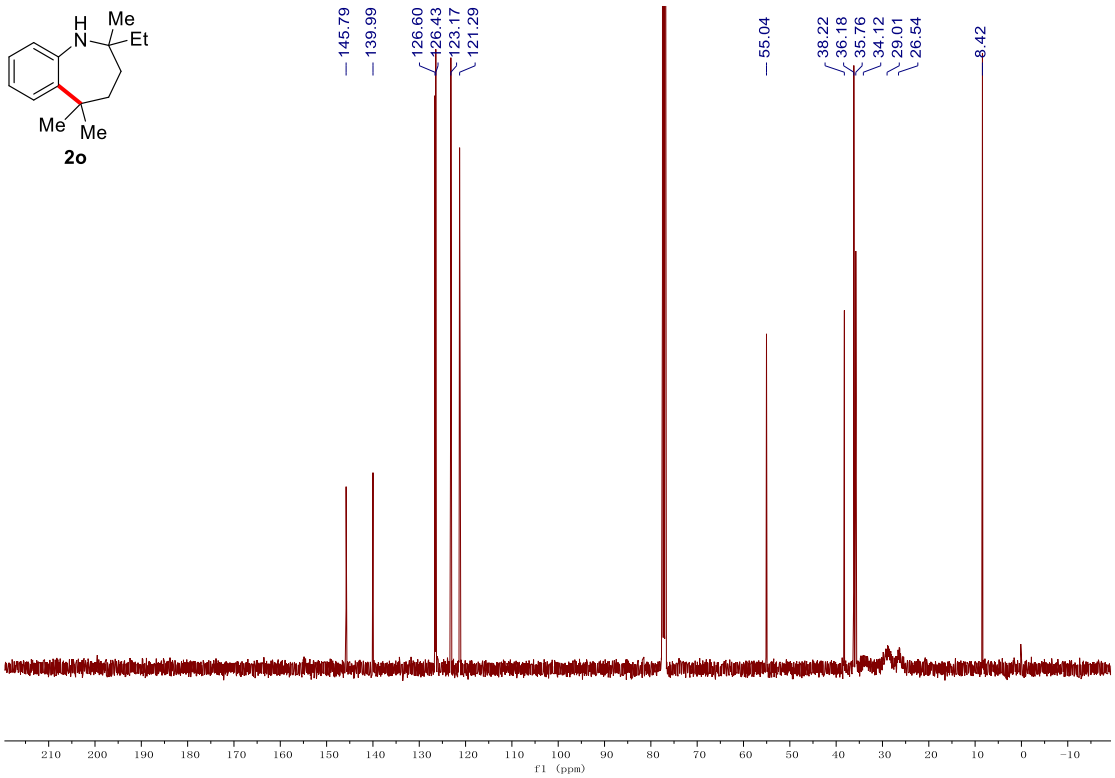

7.18
7.16
6.96
6.94
6.92
6.56
6.54
6.45
6.43
6.25
6.23
6.20
6.19
MeO
H
N
Me
Me
Me
Me
2m
+
OMe
Me
Me
Me
Me
2m'
1.01
1.02
1.02
0.98
1.04
0.99
3.12
3.00
6.94
6.10
6.35
6.35
5.36
f1 (ppm)

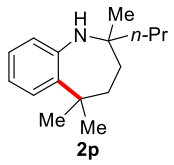

160.67
158.02
147.29
145.39
132.76
127.55
127.38
126.48
117.57
108.86
106.70
105.72
55.74
55.36
55.16
52.86
40.00
39.71
38.20
37.54
36.87
34.61
30.66
29.41
MeO
H
N
Me
Me
Me
Me
2m
+
OMe
Me
Me
Me
Me
2m'
f1 (ppm)


Me
H
N
Me
Me
Me
Me
2n
7.20
7.18
7.01
6.99
6.83
6.81
6.80
3.26
2.23
1.75
1.66
1.40
1.14
1.02
1.00
1.00
1.00
3.04
2.18
2.17
6.16
6.05
f1 (ppm)


Me
H
N
Me
Me
Me
Me
2n
144.70
140.30
128.44
128.02
124.83
120.71
52.85
38.57
38.29
36.60
28.99
19.29
f1 (ppm)

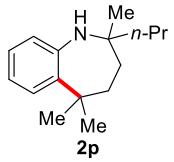

7.28
7.28
7.26
7.26
7.03
7.02
7.01
7.00
6.99
6.98
6.91
6.90
6.89
6.88
6.87
6.87
6.63
6.61
6.61
1.72
1.66
1.42
1.41
1.37
1.36
1.04
0.90
0.88
0.86
Me
Et
H
N
Me
Me
2o
1.15
0.99
1.00
1.01
1.02
1.99
2.09
2.04
6.19
3.01
3.13
f1 (ppm)


Me
Et
H
N
Me
Me
2o
145.79
139.99
126.60
126.43
123.17
121.29
55.04
38.22
36.18
35.76
34.12
29.01
26.54
8.42
f1 (ppm)


H
N
Me
n-Pr
Me
Me

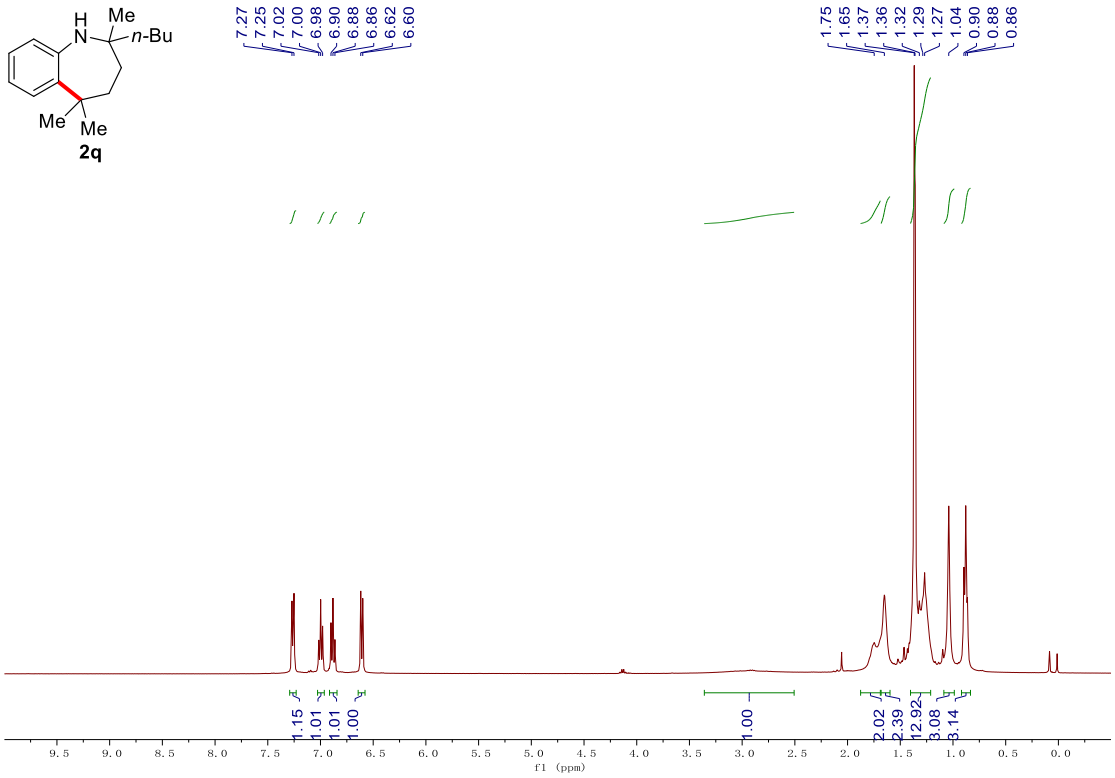
2p

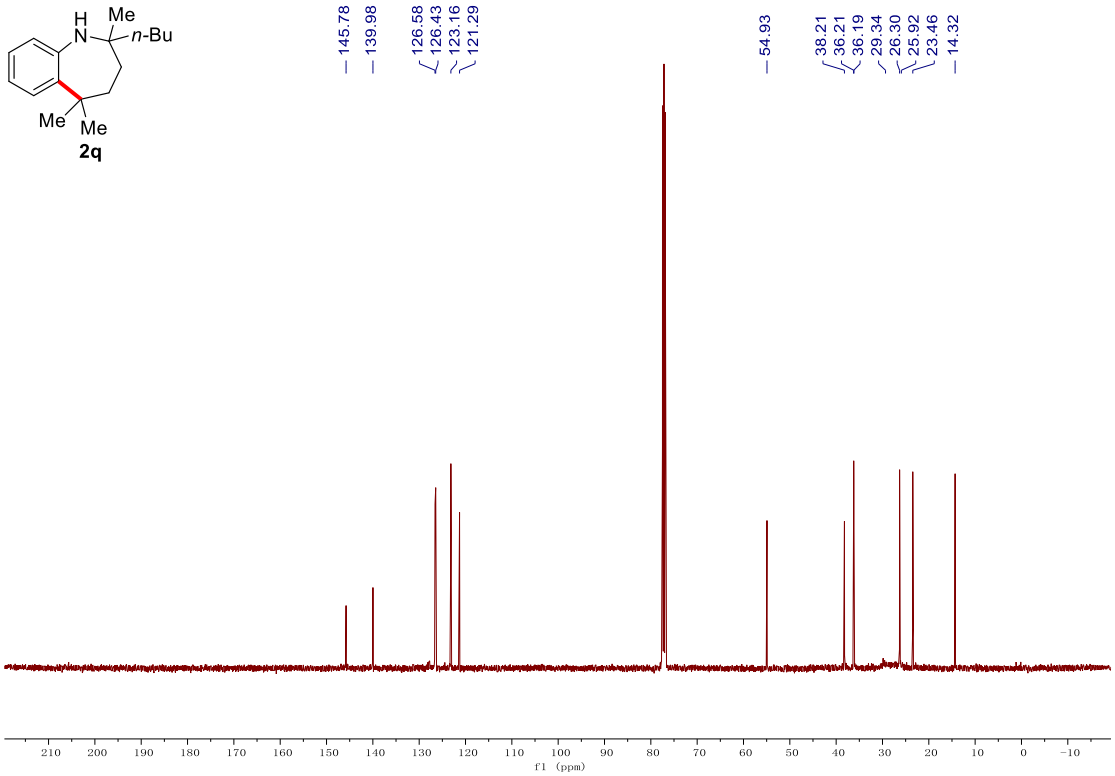
7.29
7.27
7.03
7.02
7.00
6.92
6.90
6.88
6.63
6.61
3.07
1.76
1.67
1.46
1.39
1.38
1.31
1.29
1.24
1.06
0.89
1.08
1.03
0.99
1.00
1.01
4.03
10.74
3.05
3.31
f1 (ppm)

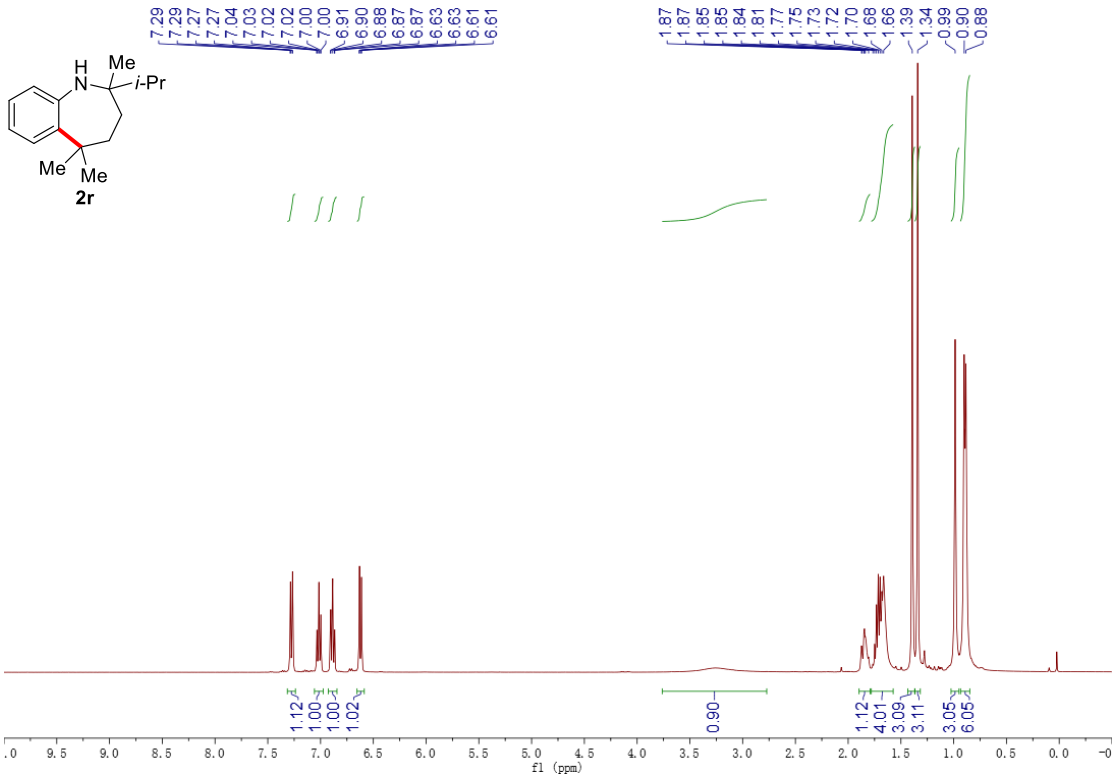

H
N
Me
n-Pr
Me
Me

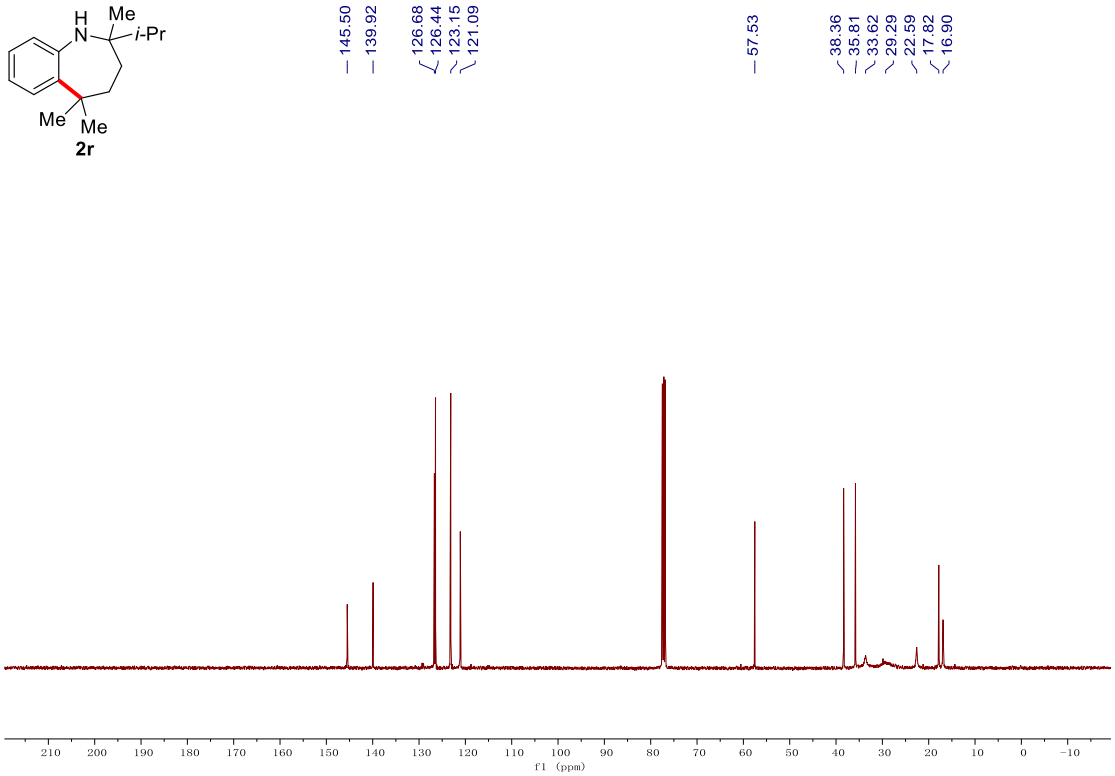
2p

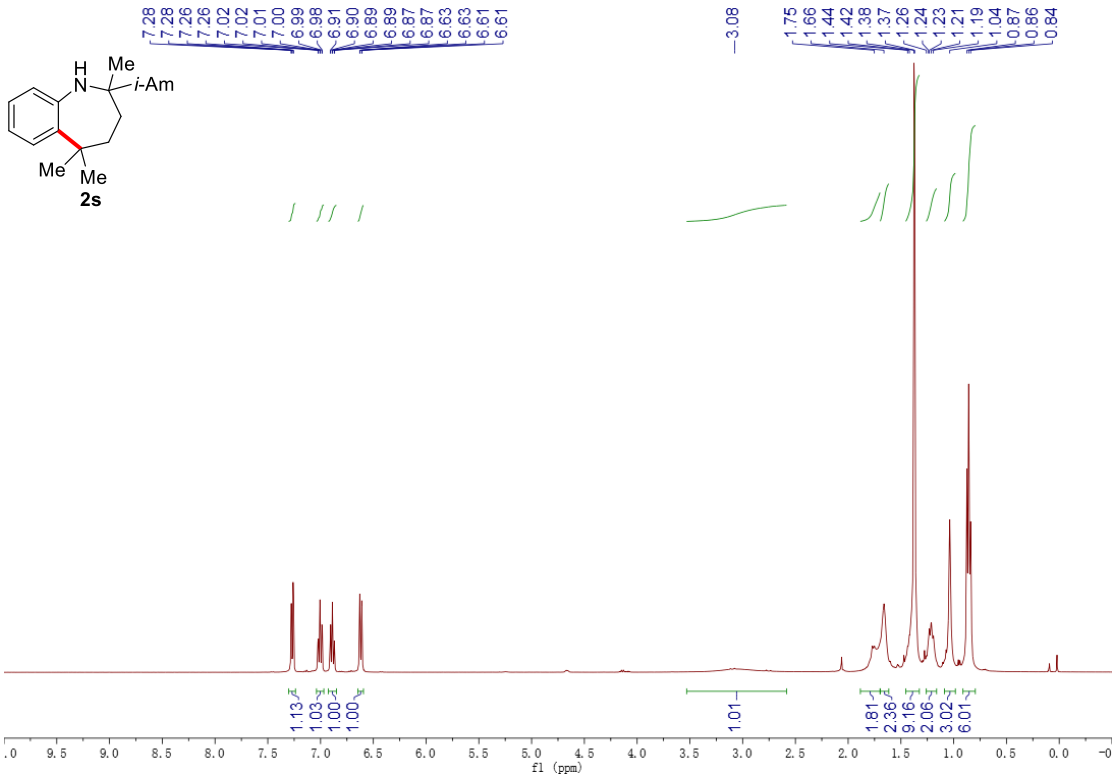
145.75
139.97
126.58
126.44
123.14
121.29
55.00
44.00
38.21
36.19
36.13
29.00
27.04
17.33
14.87
f1 (ppm)

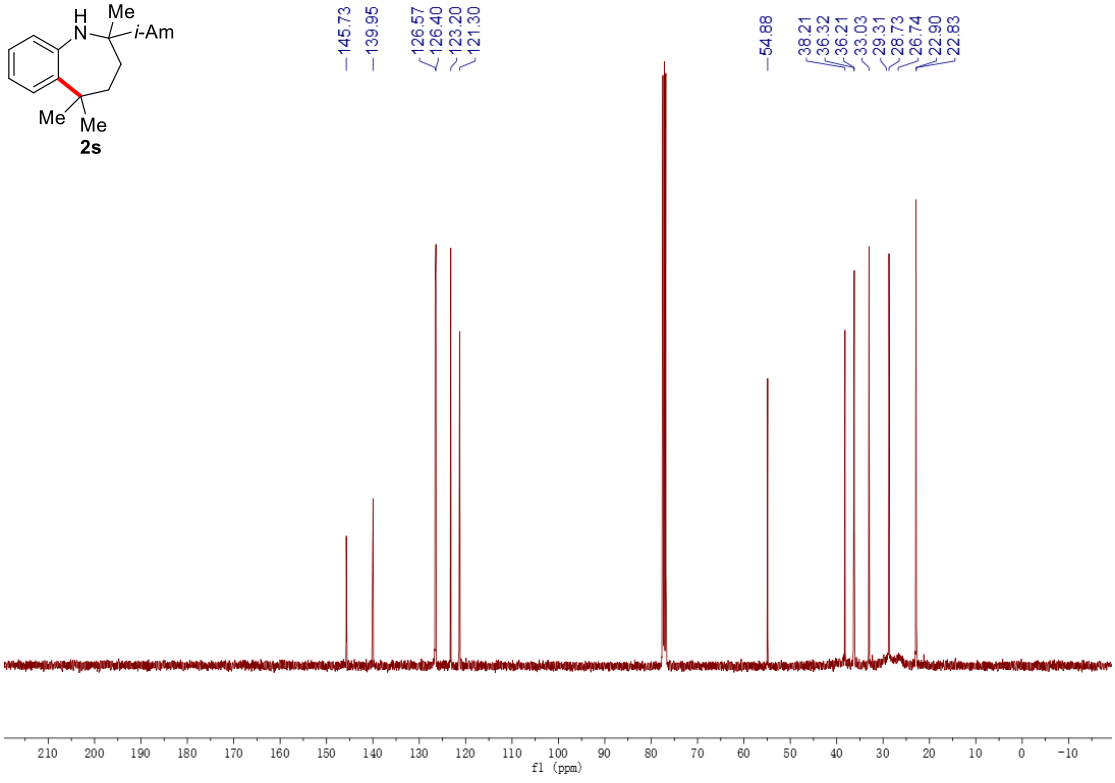

H
N
Me
n-Bu
Me
Me
2q
7.27
7.25
7.02
7.00
6.98
6.90
6.88
6.86
6.62
6.60
1.75
1.65
1.37
1.36
1.32
1.29
1.27
1.04
0.90
0.88
0.86
1.15
1.01
1.01
1.00
1.00
2.02
2.39
12.92
3.08
3.14
f1 (ppm)

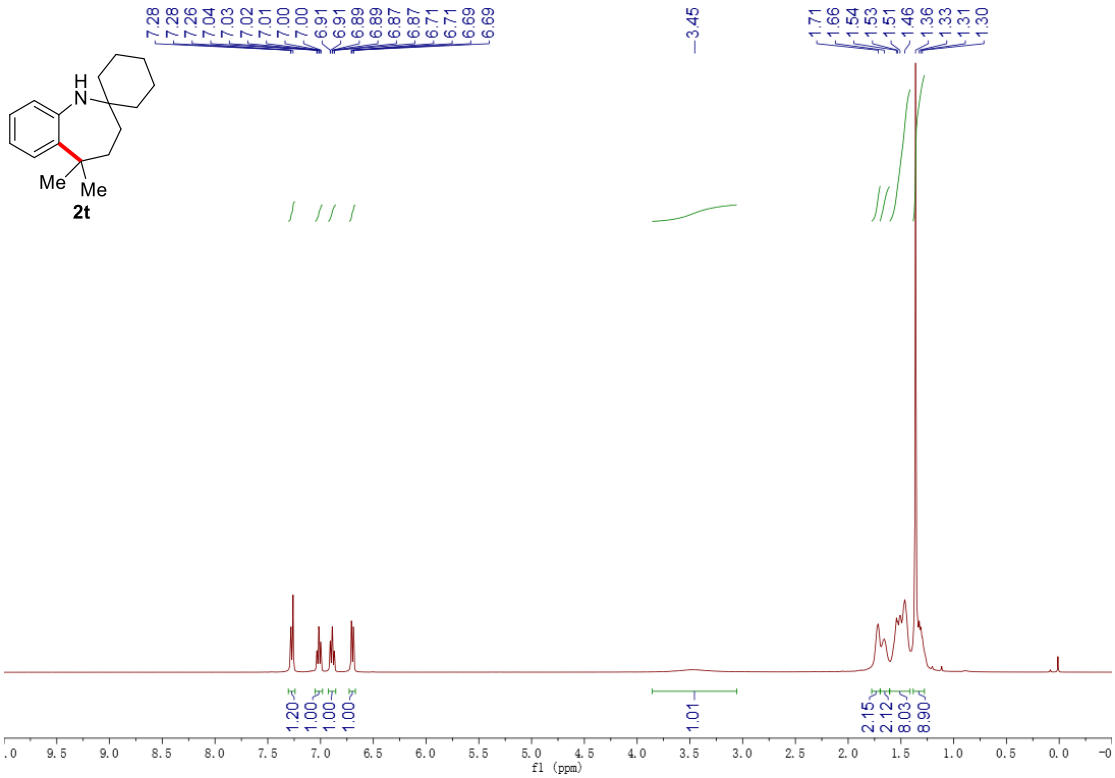

H
N
Me
n-Bu
Me
Me
2q
145.78
139.98
126.58
126.43
123.16
121.29
54.93
38.21
36.21
36.19
29.34
26.30
25.92
23.46
14.32
f1 (ppm)

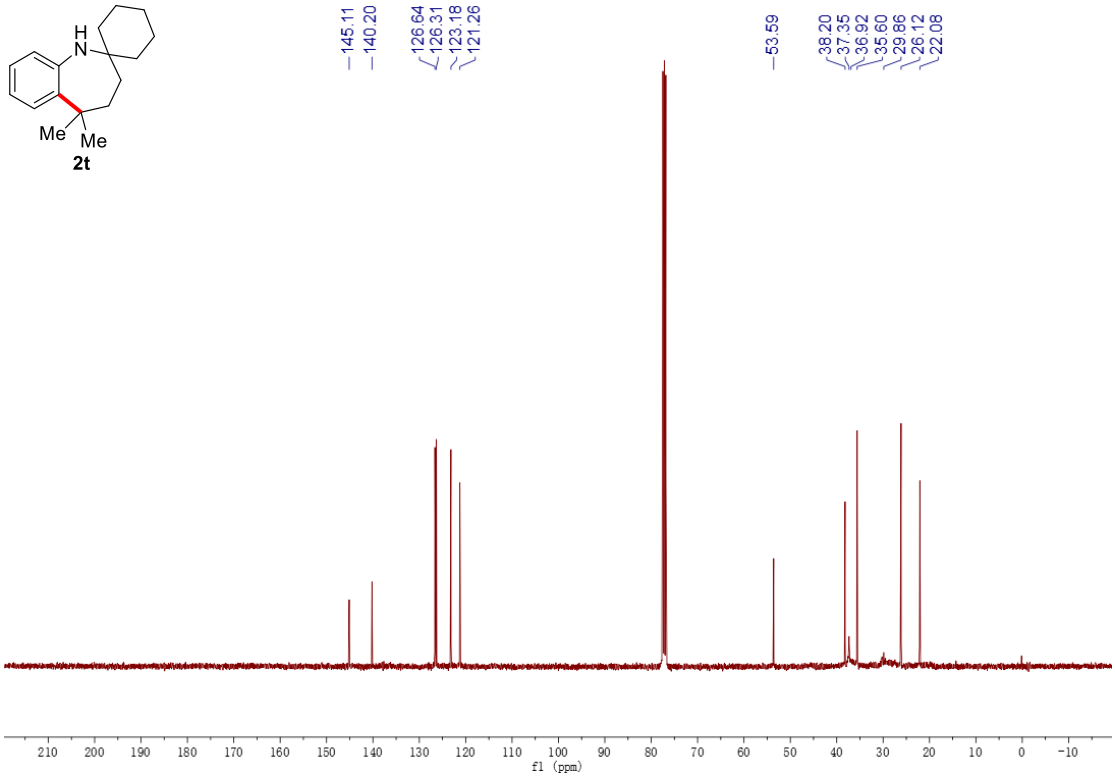

7.29
7.29
7.27
7.27
7.04
7.03
7.02
7.02
7.00
7.00
6.91
6.90
6.88
6.87
6.87
6.63
6.63
6.61
6.61
1.87
1.87
1.85
1.85
1.84
1.81
1.77
1.75
1.73
1.72
1.70
1.68
1.66
1.39
1.34
0.99
0.90
0.88
H
N
Me
i-Pr
Me
Me
2r
1.12
1.00
1.00
1.02
0.90
1.12
4.01
3.09
3.11
3.05
6.05
f1 (ppm)

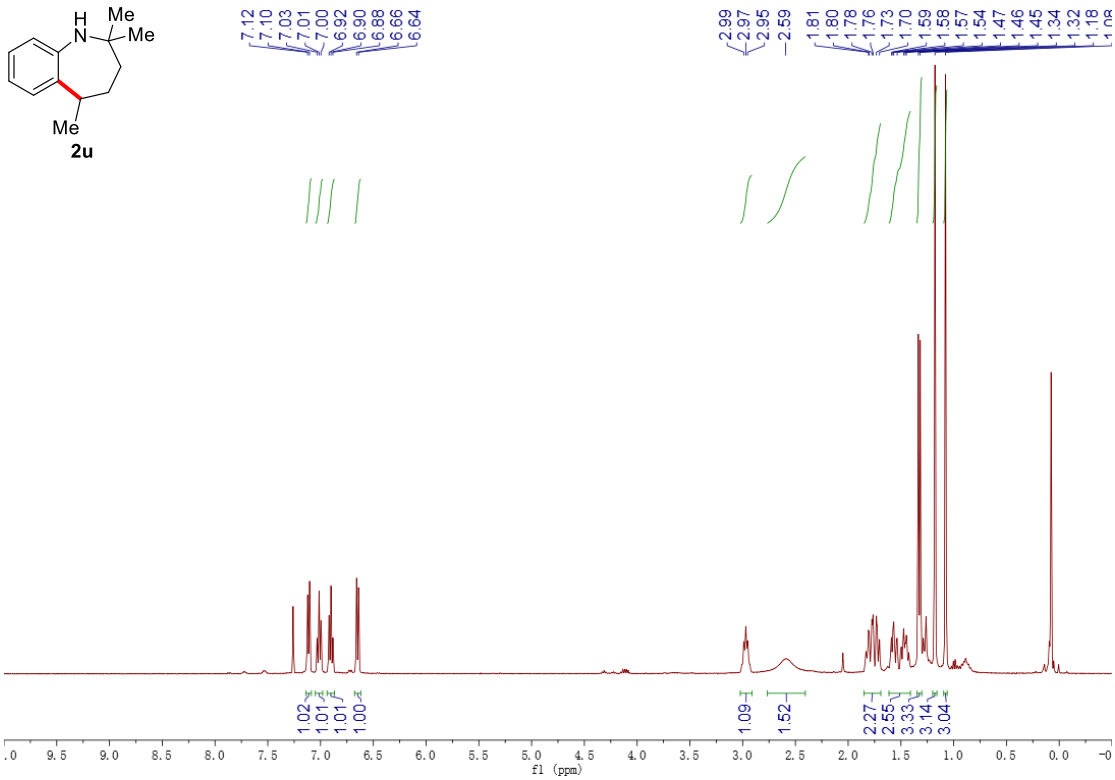

145.50
139.92
126.68
126.44
123.15
121.09
57.53
38.36
35.81
33.62
29.29
22.59
17.82
16.90
H
N
Me
i-Pr
Me
Me
2r
f1 (ppm)

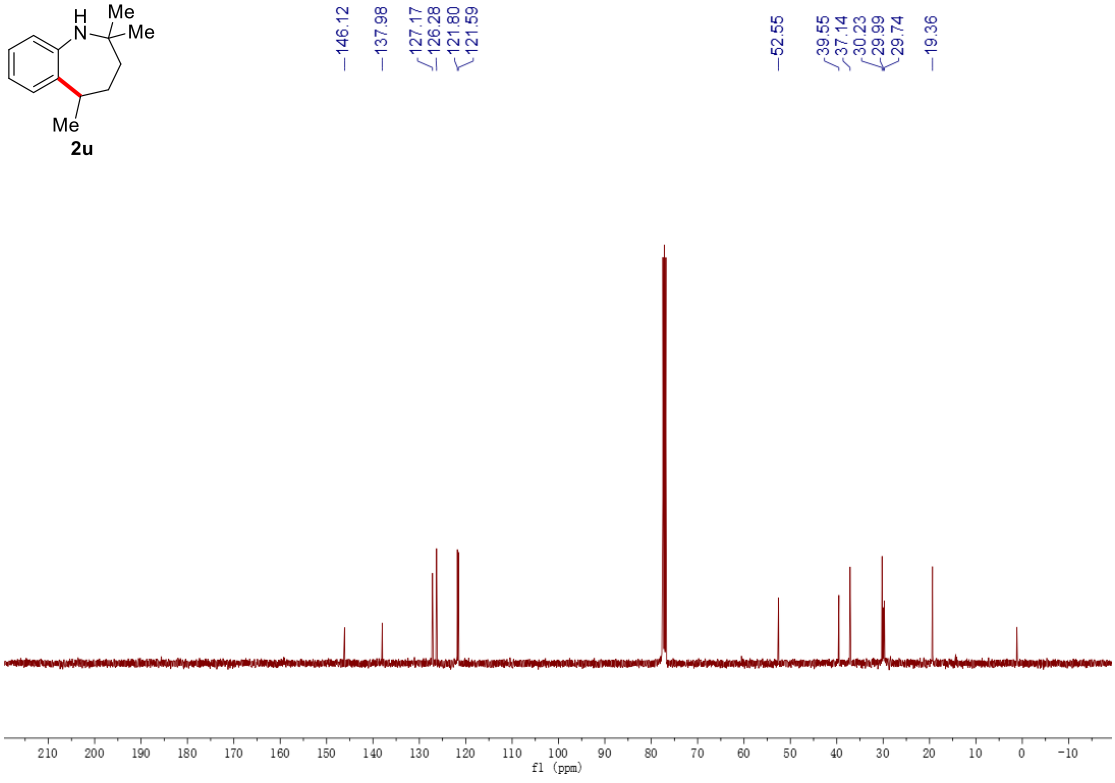

7.28
7.28
7.26
7.26
7.26
7.02
7.02
7.01
7.00
6.99
6.98
6.91
6.90
6.89
6.89
6.87
6.87
6.63
6.63
6.61
6.61
3.08
1.75
1.66
1.44
1.42
1.38
1.37
1.26
1.24
1.23
1.21
1.19
1.04
0.87
0.86
0.84
H
N
Me
i-Am
Me
Me
2s
1.13
1.03
1.00
1.00
1.01
1.81
2.36
9.16
2.06
3.02
6.01
f1 (ppm)

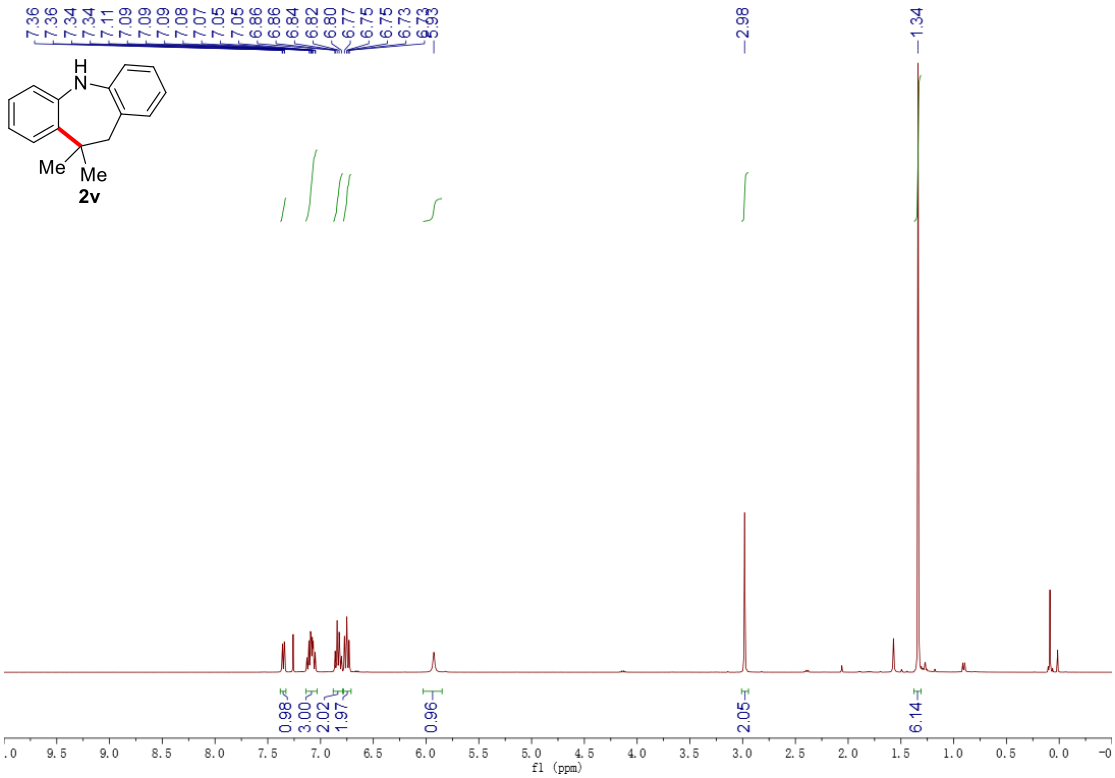

145.73
139.95
126.57
126.40
123.20
121.30
54.88
38.21
36.32
36.21
33.03
29.31
28.73
26.74
22.90
22.83
H
N
Me
i-Am
Me
Me
2s
f1 (ppm)

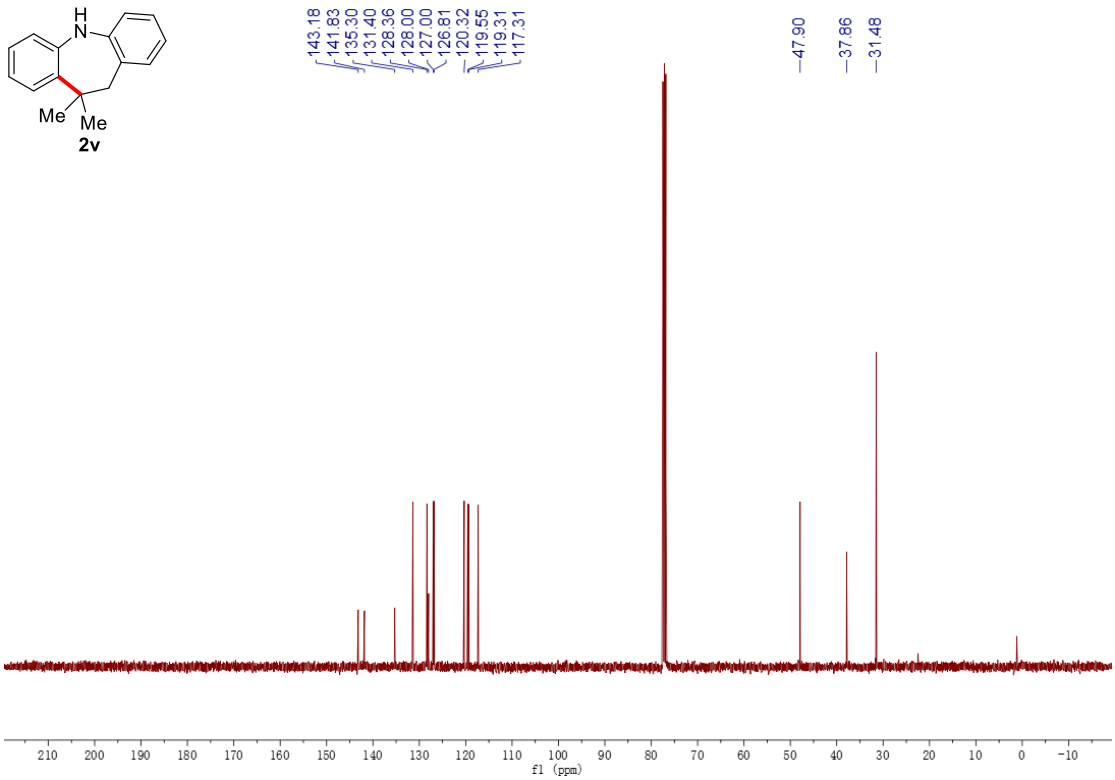

7.28
7.28
7.26
7.04
7.03
7.02
7.01
7.00
7.00
6.91
6.91
6.89
6.89
6.87
6.87
6.71
6.71
6.69
6.69
3.45
1.71
1.66
1.54
1.53
1.51
1.46
1.36
1.33
1.31
1.30
H
N
Me
Me
2t
1.20
1.00
1.00
1.00
1.01
2.15
2.12
8.03
8.90
f1 (ppm)

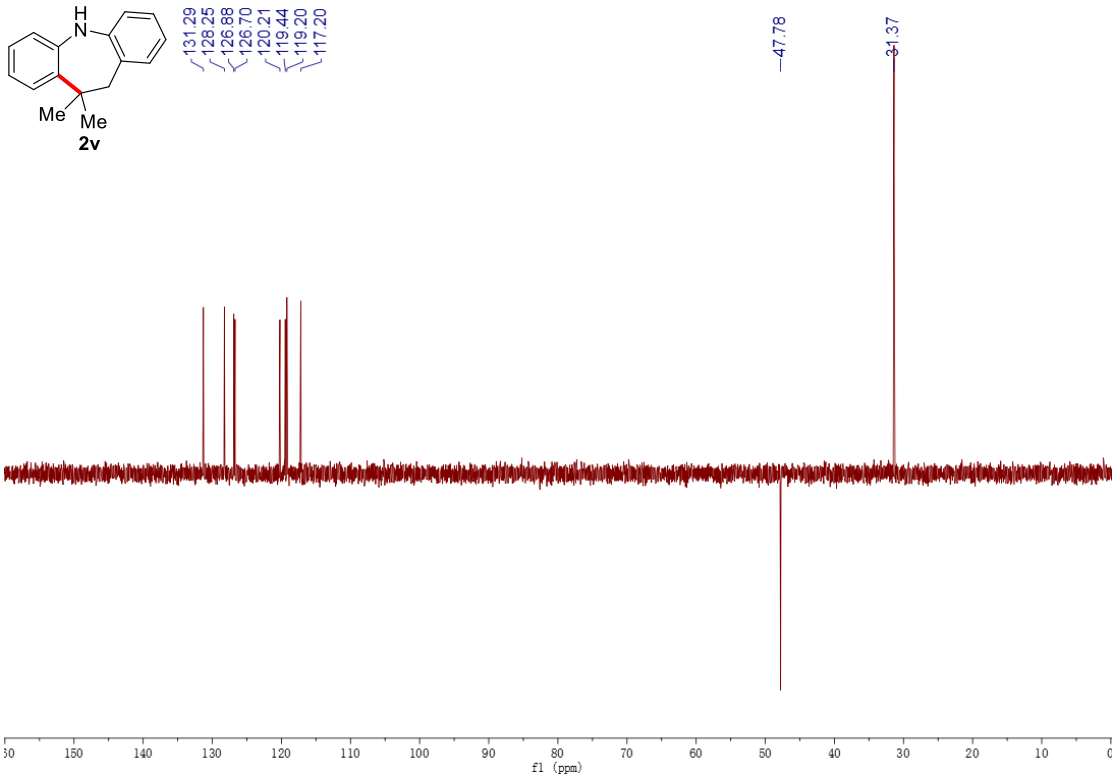

145.11
140.20
126.64
126.31
123.18
121.26
53.59
38.20
37.35
36.92
35.60
29.86
26.12
22.08
H
N
Me
Me
2t
f1 (ppm)

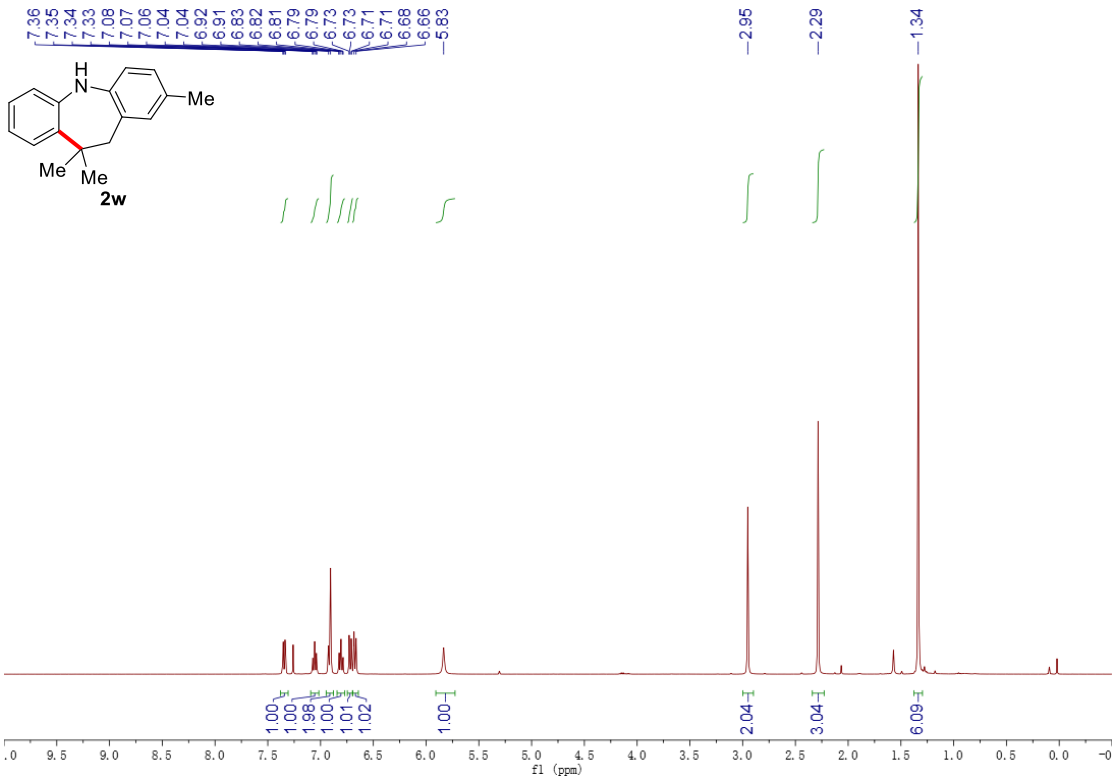

Me
H
N
Me
Me
2u
7.12
7.10
7.03
7.01
7.00
6.92
6.90
6.88
6.66
6.64
2.99
2.97
2.95
2.59
1.81
1.80
1.78
1.76
1.73
1.70
1.59
1.58
1.57
1.54
1.47
1.46
1.45
1.34
1.32
1.18
1.02
1.01
1.01
1.00
1.09
1.52
2.27
2.55
3.33
3.14
3.04
f1 (ppm)

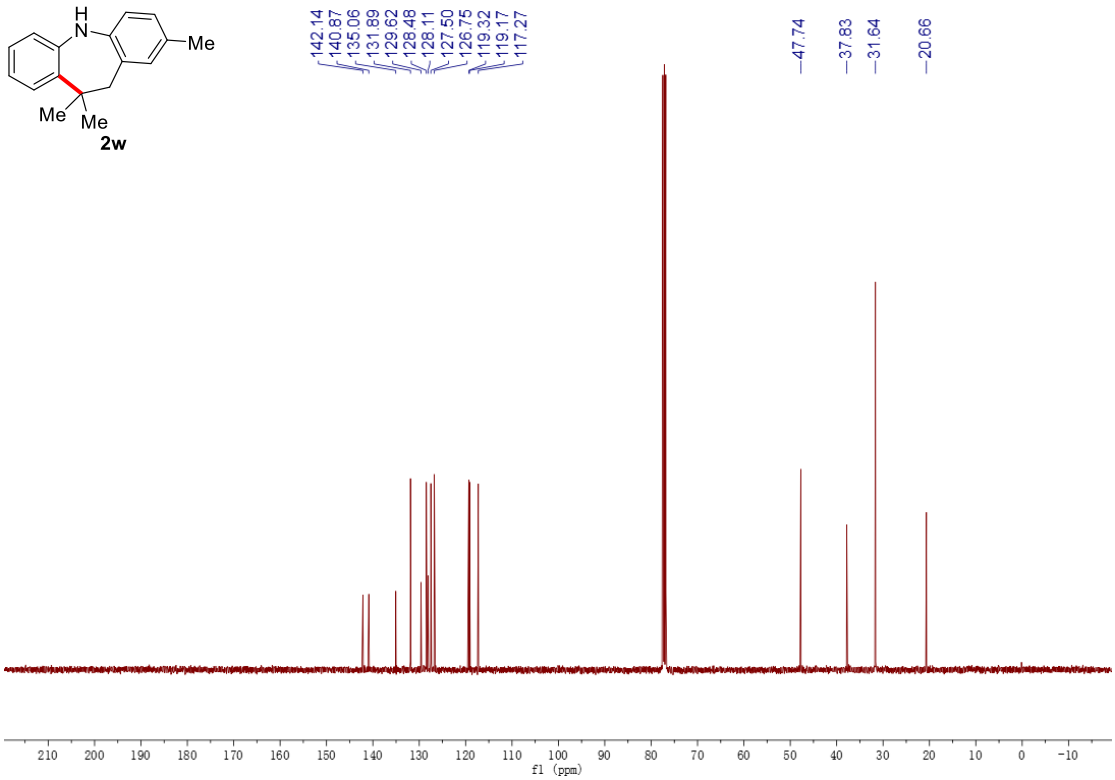

Me
H
N
Me
Me
2u
146.12
137.98
127.17
126.28
121.80
121.59
52.55
39.55
37.14
30.23
29.99
29.74
19.36
f1 (ppm)

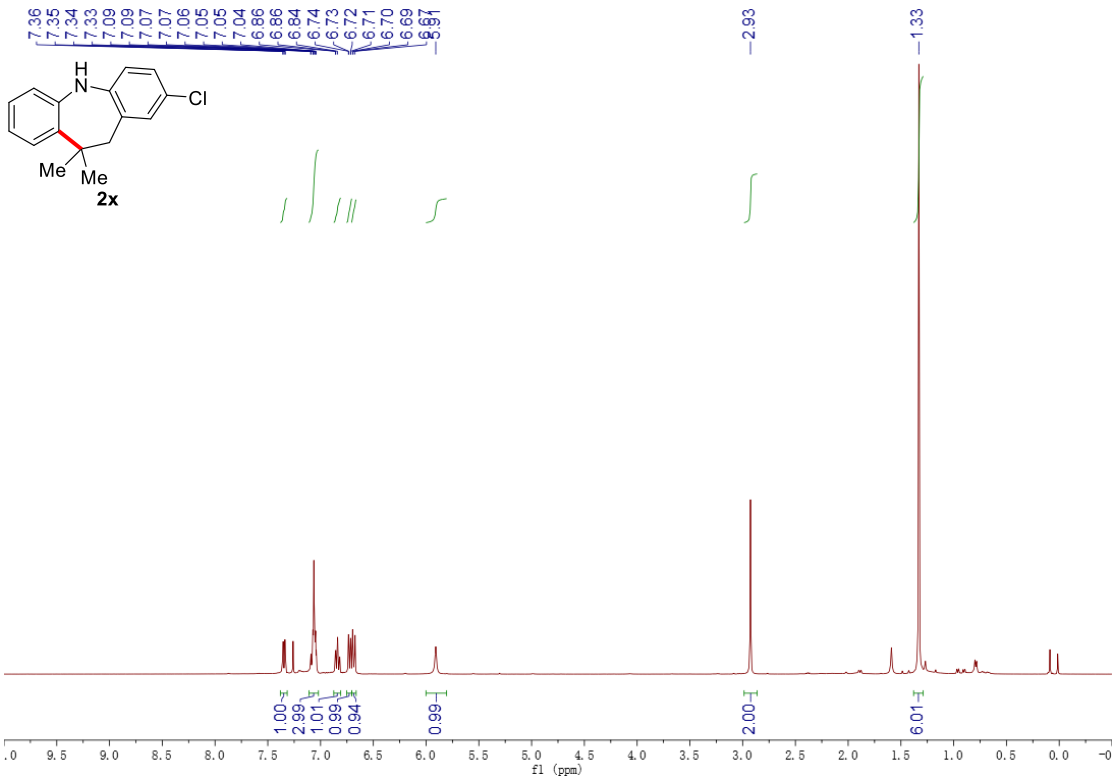

7.36
7.36
7.34
7.34
7.11
7.09
7.09
7.09
7.08
7.07
7.05
7.05
6.86
6.84
6.82
6.80
6.77
6.75
6.73
6.73
2.98
1.34
H
N
Me
Me
2v
0.98
3.00
2.02
1.97
0.96
2.05
6.14
f1 (ppm)

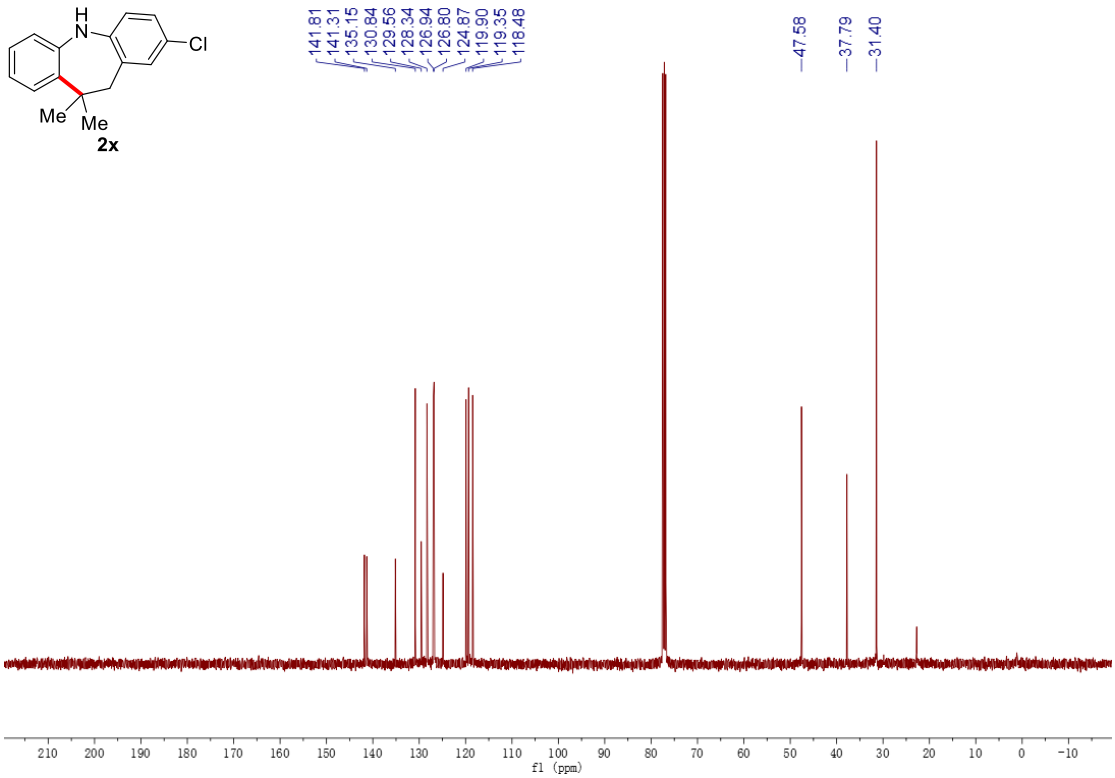

143.18
141.83
135.30
131.40
128.36
128.00
127.00
126.81
120.32
119.55
119.31
117.31
47.90
37.86
31.48
H
N
Me
Me
2v
f1 (ppm)

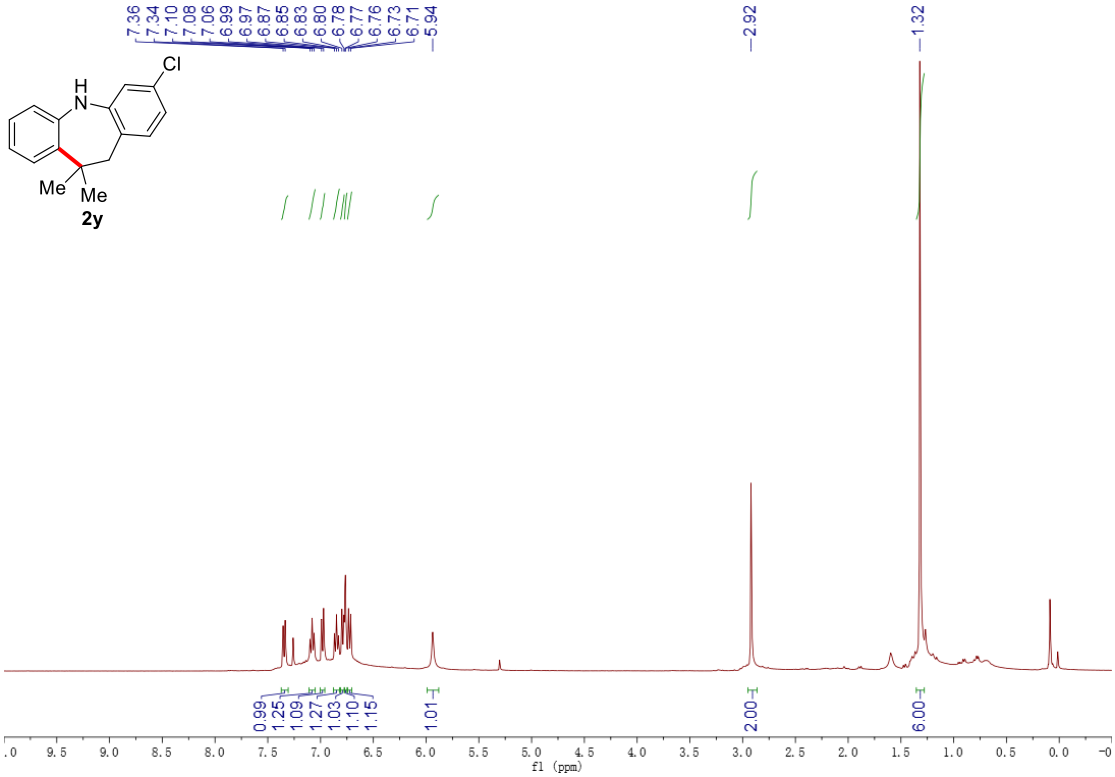

131.29
128.25
126.88
126.70
120.21
119.44
119.20
117.20
47.78
31.37
Me
Me
2v
f1 (ppm)

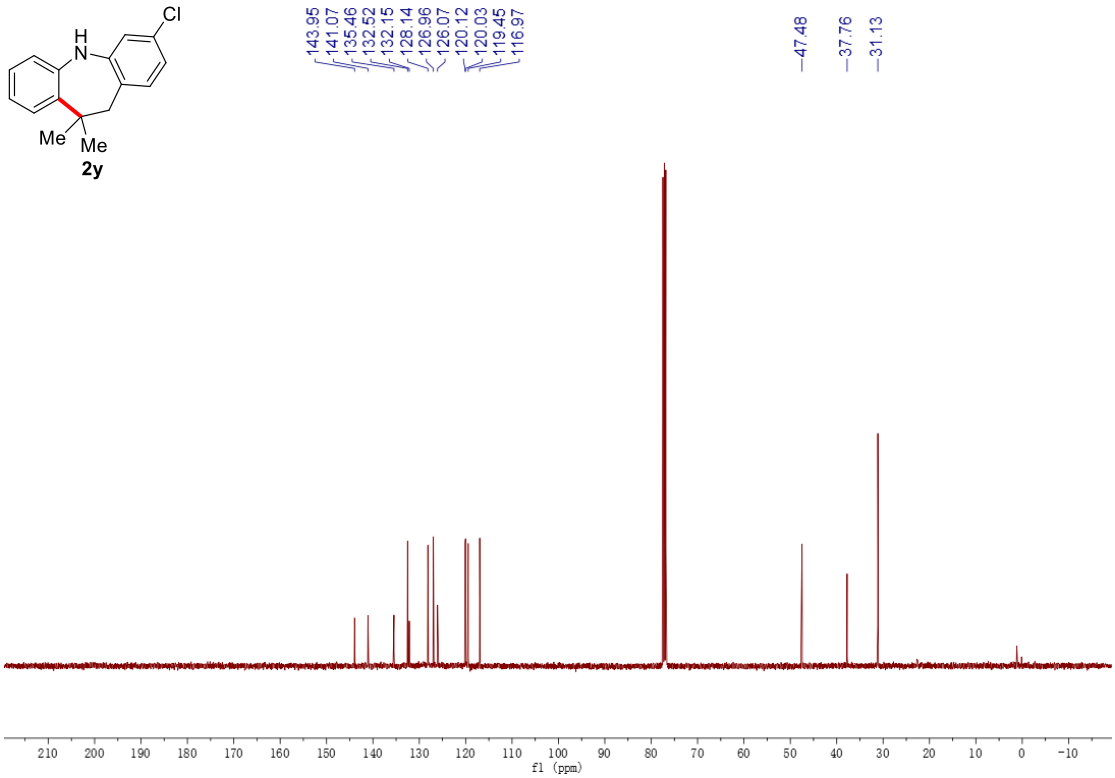

7.36
7.35
7.34
7.33
7.08
7.07
7.06
7.04
7.04
6.92
6.91
6.83
6.82
6.81
6.79
6.79
6.73
6.73
6.71
6.71
6.68
6.66
5.83
2.95
2.29
1.34
Me
Me
Me
2w
1.00
1.00
1.98
1.00
1.01
1.02
1.00
2.04
3.04
6.09
f1 (ppm)

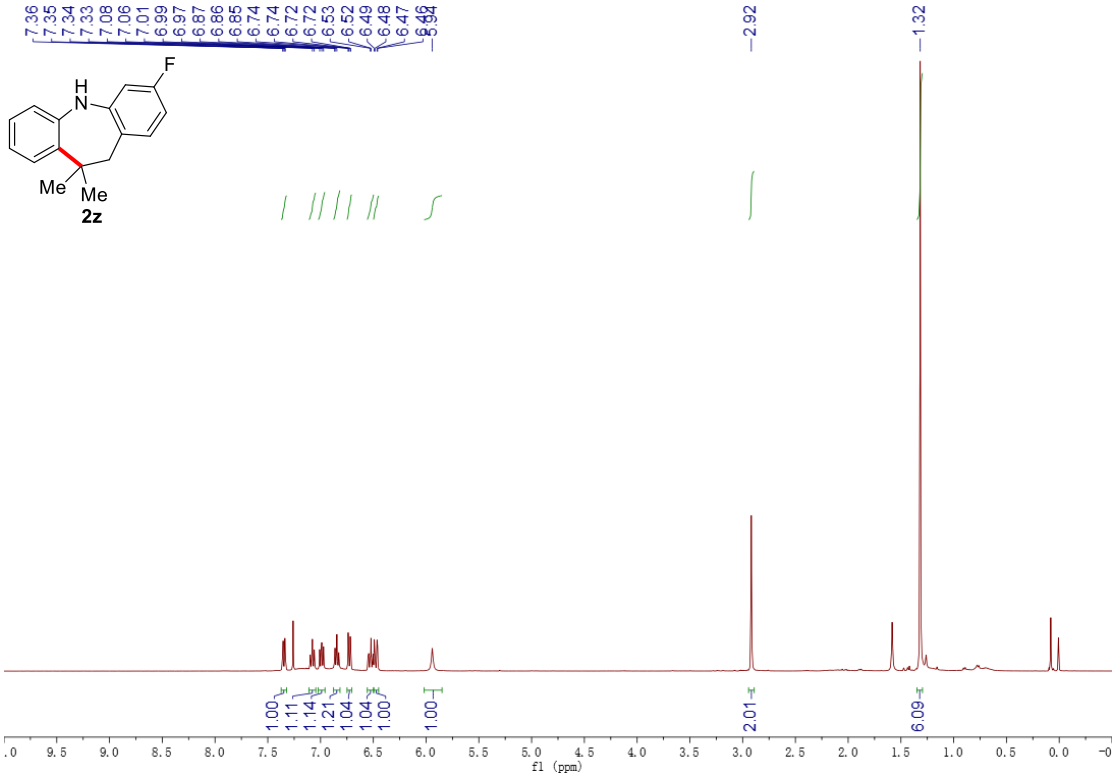

H
N
Me
Me
Me
2w
142.14
140.87
135.06
131.89
129.62
128.48
128.11
127.50
126.75
119.32
119.17
117.27
47.74
37.83
31.64
20.66
f1 (ppm)

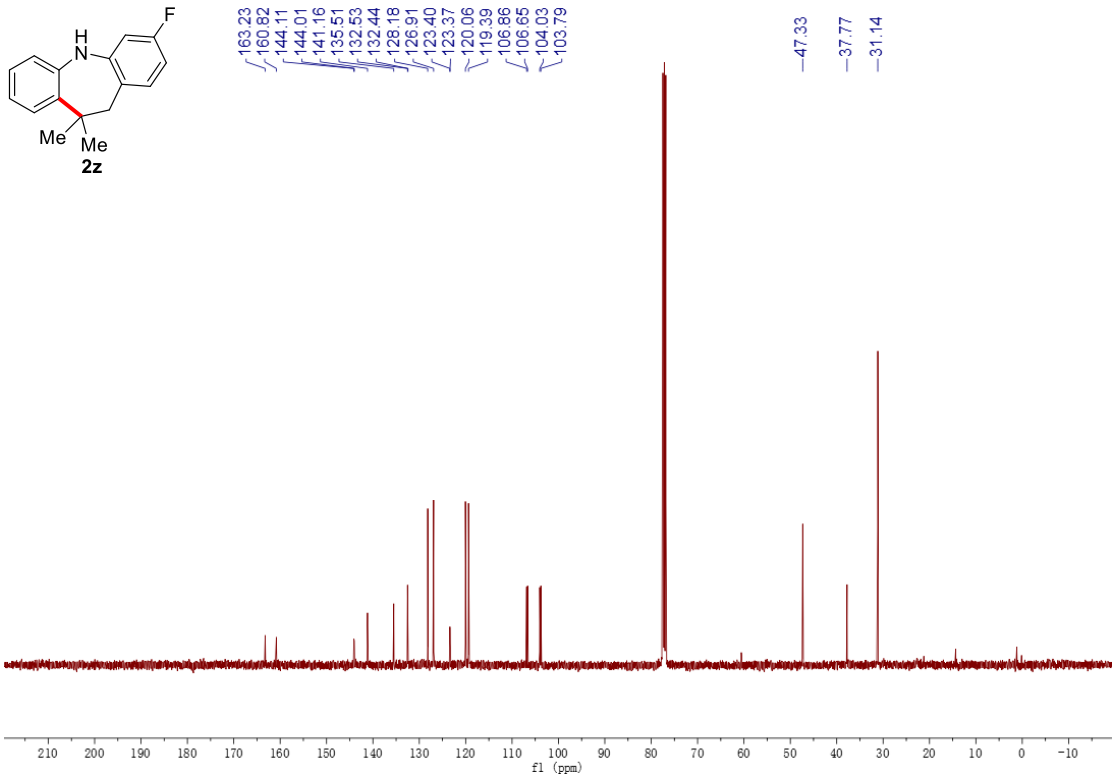

7.36
7.35
7.34
7.33
7.09
7.09
7.07
7.07
7.06
7.05
7.05
7.04
6.86
6.86
6.84
6.74
6.73
6.72
6.71
6.70
6.69
2.93
1.33
H
N
Cl
Me
Me
2x
1.00
2.99
1.01
0.99
0.94
0.99
2.00
6.01
f1 (ppm)

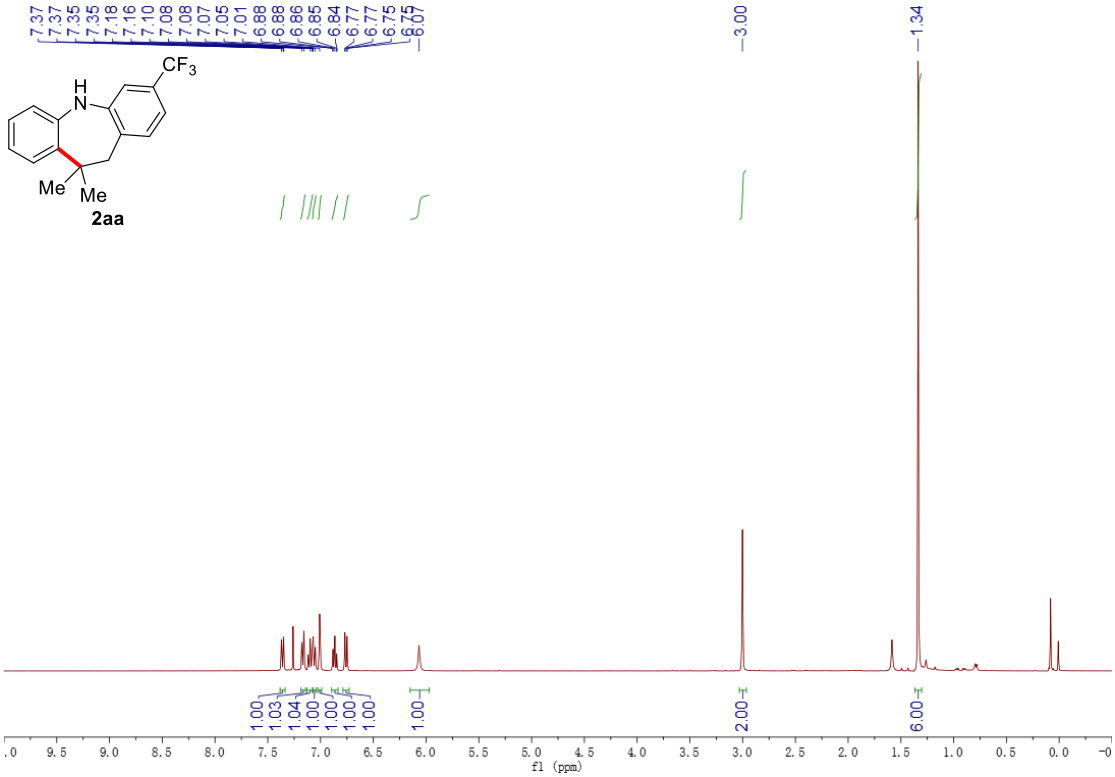

H
N
Cl
Me
Me
2x
141.81
141.31
135.15
130.84
129.56
128.34
126.94
126.80
124.87
119.90
119.35
118.48
47.58
37.79
31.40
f1 (ppm)

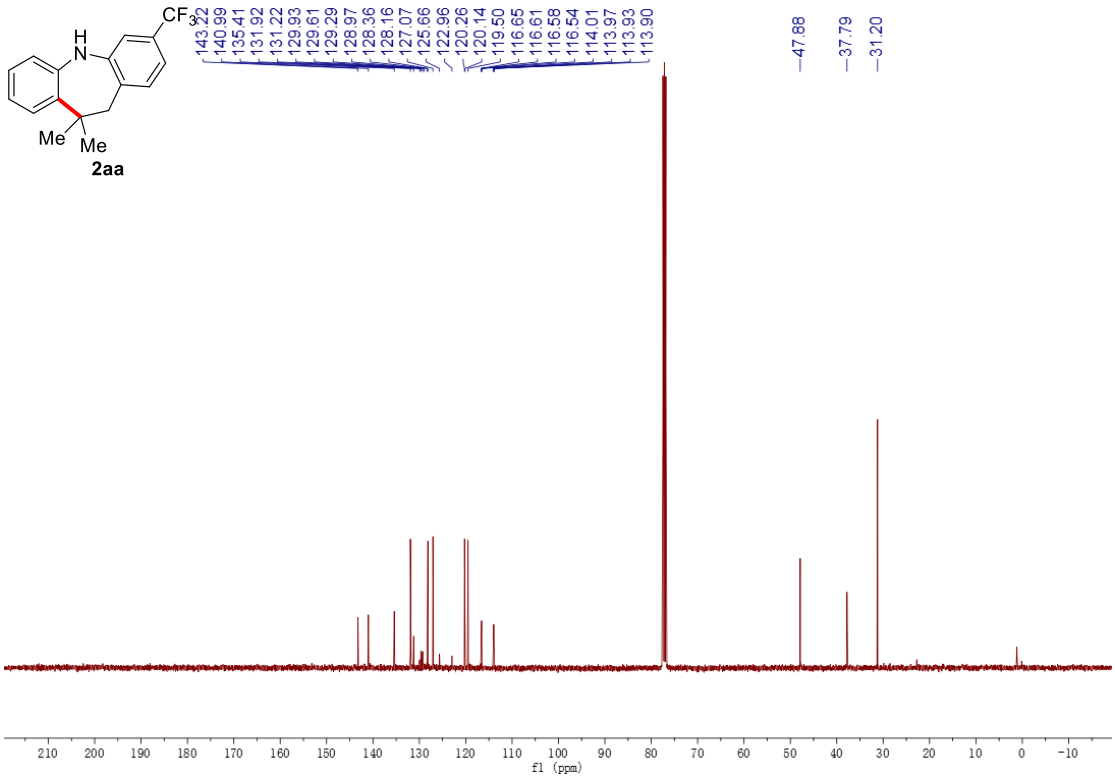

H
N
Cl
Me
Me
2y
7.36
7.34
7.10
7.08
7.06
6.99
6.97
6.87
6.85
6.83
6.80
6.78
6.77
6.76
6.73
6.71
5.94
2.92
1.32
0.99
1.25
1.09
1.27
1.03
1.10
1.15
1.01
2.00
6.00
f1 (ppm)

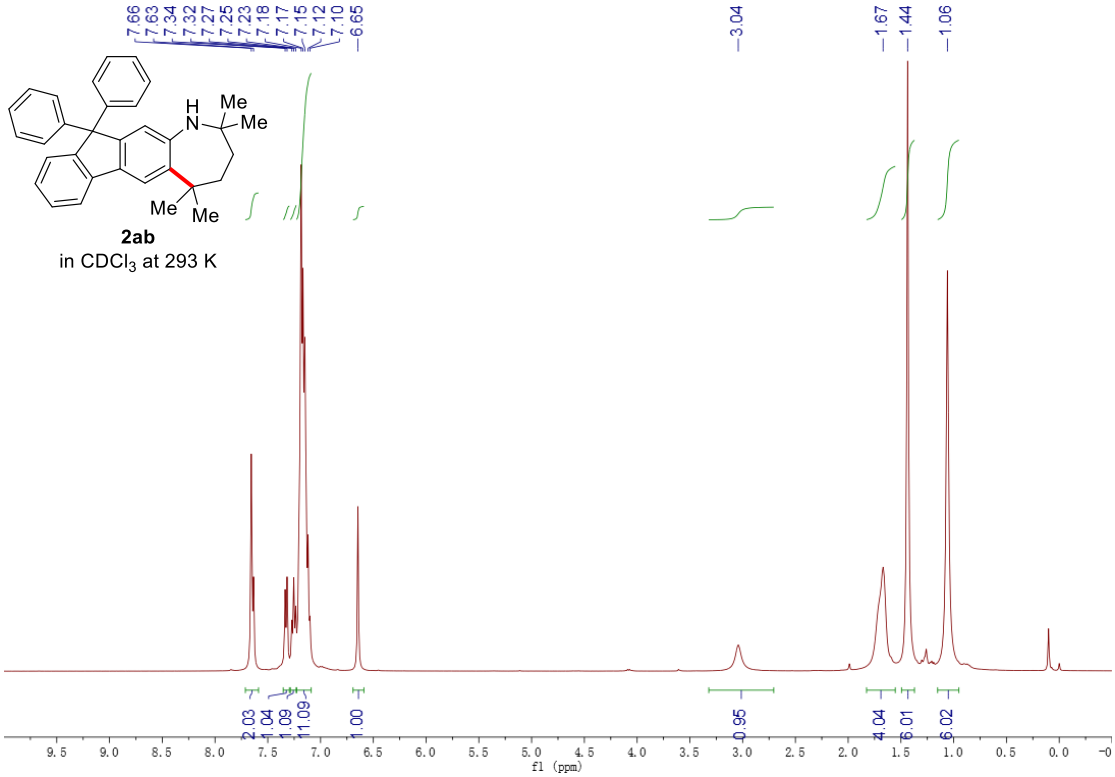

Cl
H
N
Me
Me
2y
143.95
141.07
135.46
132.52
132.15
128.14
126.96
126.07
120.12
120.03
119.45
116.97
47.48
37.76
31.13
f1 (ppm)

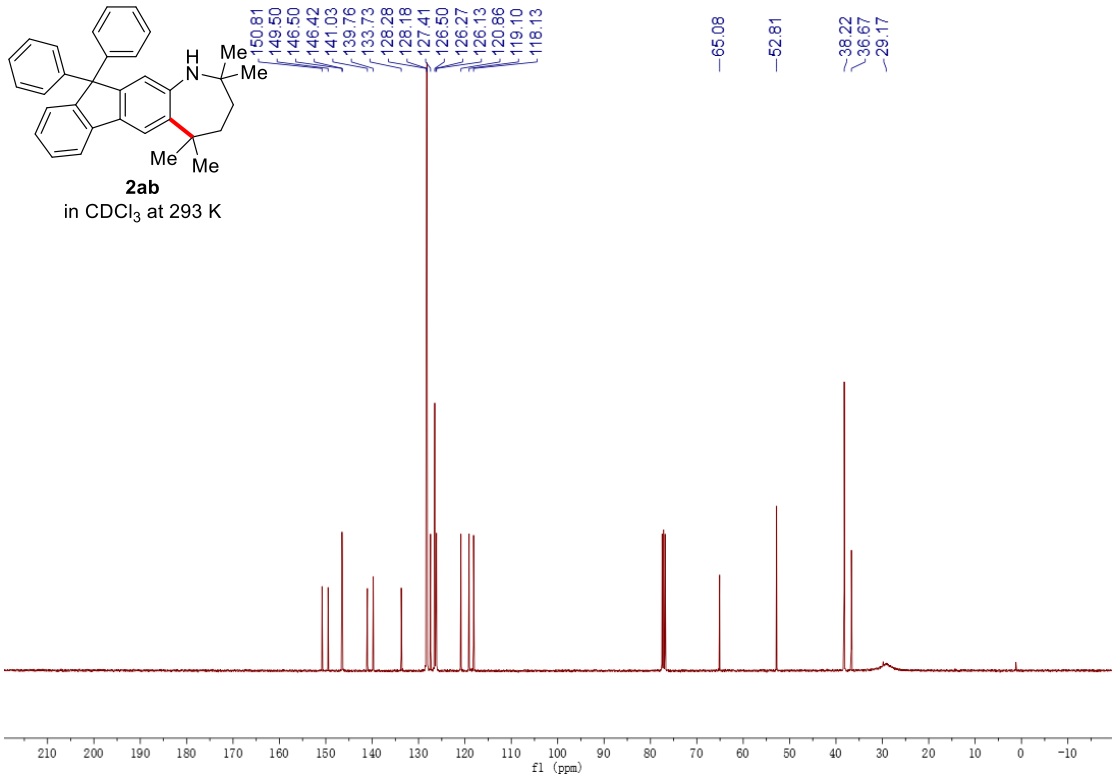

7.36
7.35
7.34
7.33
7.08
7.06
7.01
6.99
6.97
6.87
6.86
6.85
6.74
6.74
6.72
6.72
6.53
6.52
6.49
6.48
6.47
6.46
5.94
2.92
1.32
F
H
N
Me
Me
2z
1.00
1.11
1.14
1.21
1.04
1.04
1.00
1.00
2.01
6.09
f1 (ppm)

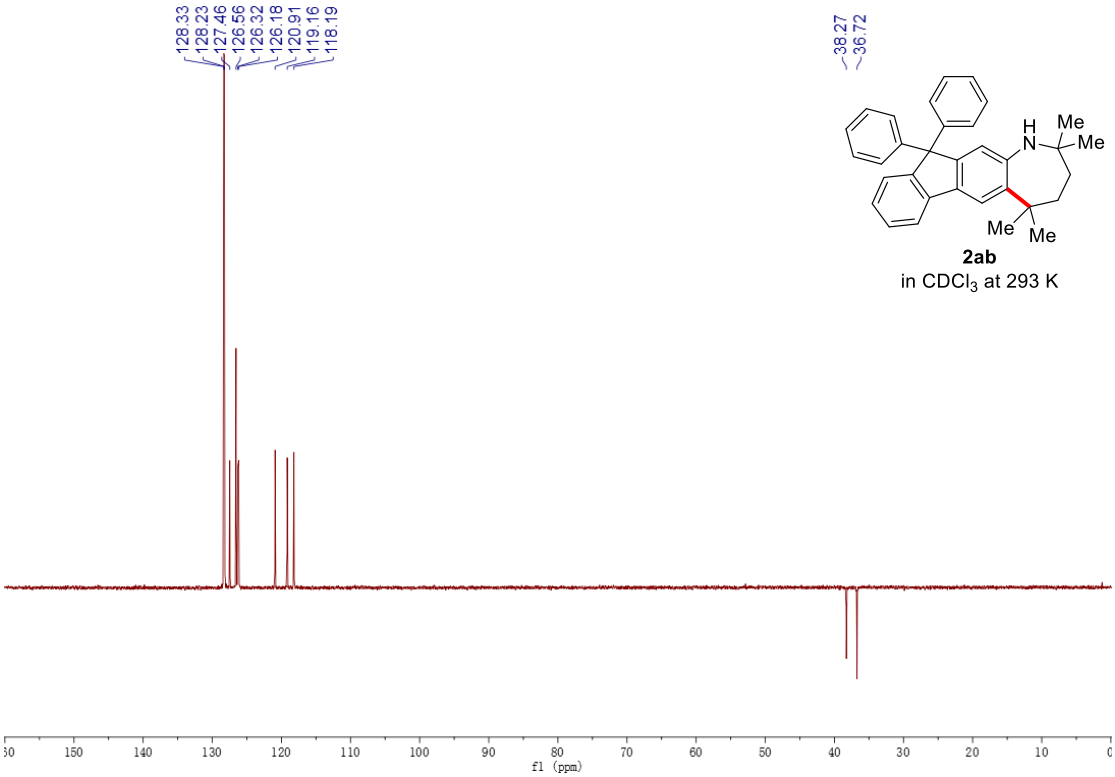

F
H
N
Me
Me
2z
163.23
160.82
144.11
144.01
141.16
135.51
132.53
132.44
128.18
126.91
123.40
123.37
120.06
119.39
106.86
106.65
104.03
103.79
47.33
37.77
31.14
f1 (ppm)

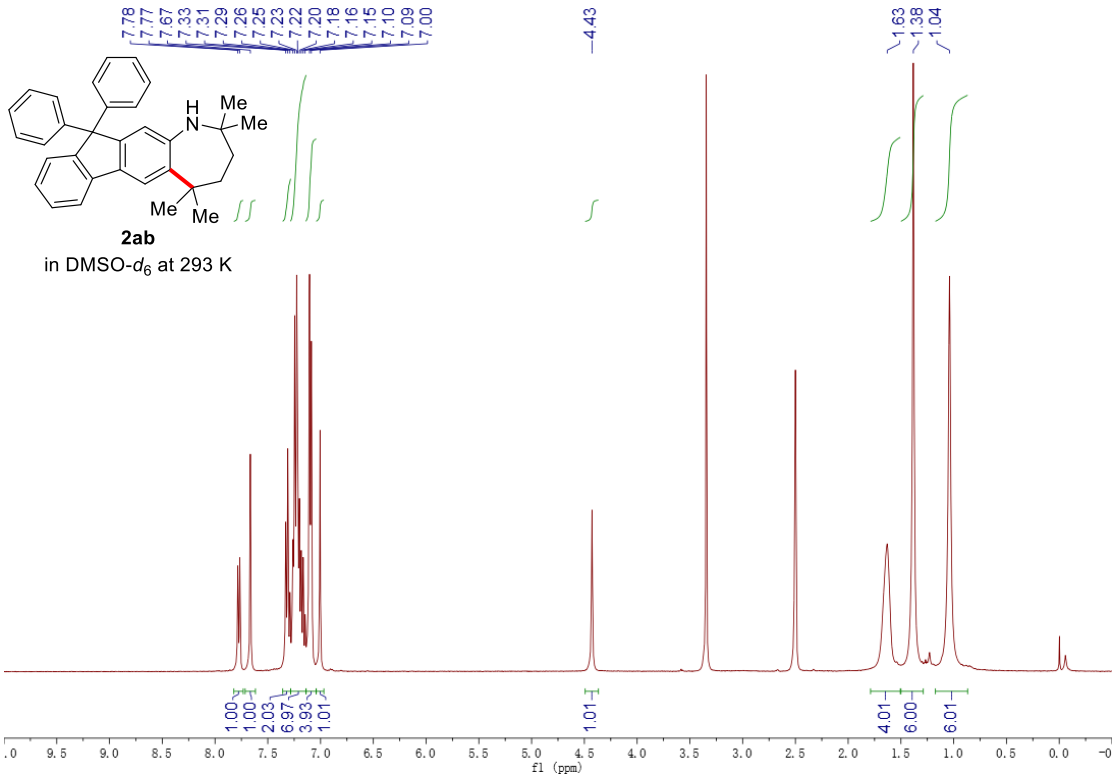

7.37
7.37
7.35
7.35
7.18
7.16
7.10
7.08
7.08
7.07
7.05
7.01
6.88
6.88
6.86
6.85
6.84
6.77
6.77
6.75
6.75
6.07
3.00
1.34
CF3
H
N
Me
Me
2aa
1.00
1.03
1.04
1.00
1.00
1.00
1.00
1.00
2.00
6.00
f1 (ppm)


CF3
H
N
Me
Me
2aa
143.22
140.99
135.41
131.92
131.22
129.93
129.61
129.29
128.97
128.36
128.16
127.07
125.66
122.96
120.26
120.14
119.50
116.65
116.61
116.58
116.54
114.01
113.97
113.93
113.90
47.88
37.79
31.20
f1 (ppm)


7.66
7.63
7.34
7.32
7.27
7.25
7.23
7.18
7.17
7.15
7.12
7.10
6.65
3.04
1.67
1.44
1.06
H
N
Me
Me
Me
Me
2ab
in CDCl3 at 293 K
2.03
1.04
1.09
11.09
1.00
0.95
4.04
6.01
6.02
f1 (ppm)

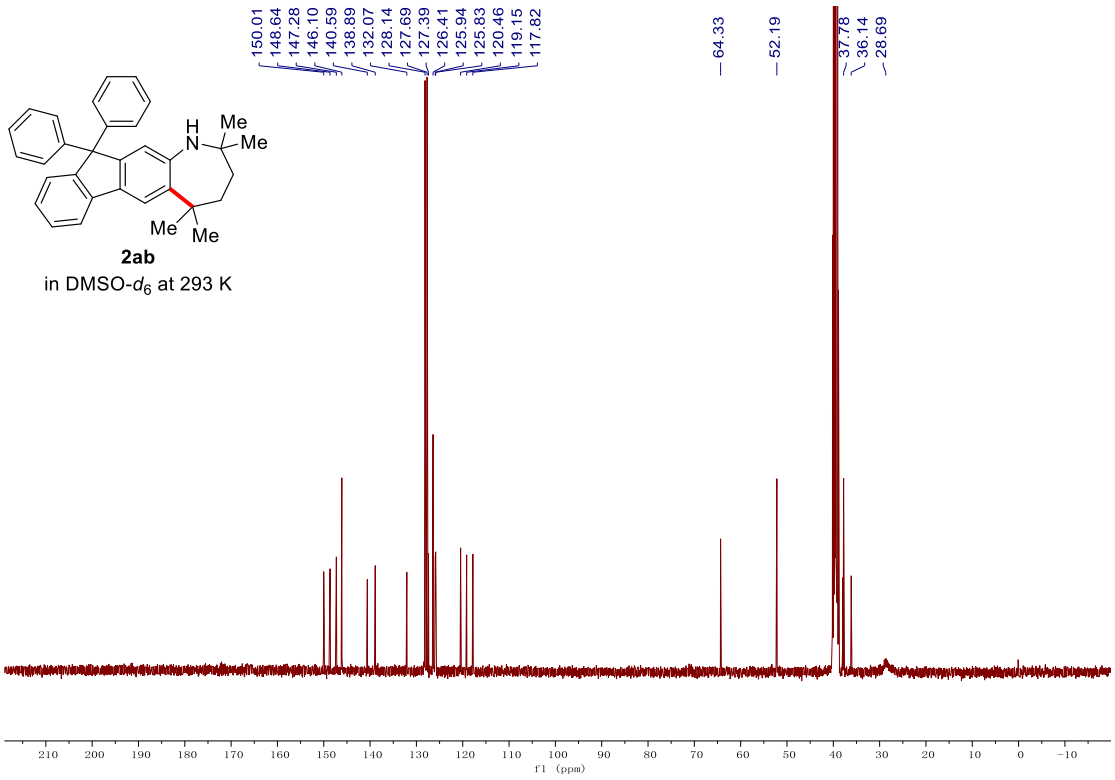

150.81
149.50
146.50
146.42
141.03
139.76
133.73
128.28
128.18
127.41
126.50
126.27
126.13
120.86
119.10
118.13
65.08
52.81
38.22
36.67
29.17
H
N
Me
Me
Me
Me
2ab
in CDCl3 at 293 K
f1 (ppm)


128.33
128.23
127.46
126.56
126.32
126.18
120.91
119.16
118.19
38.27
36.72
H
N
Me
Me
Me
Me
2ab
in CDCl3 at 293 K
f1 (ppm)



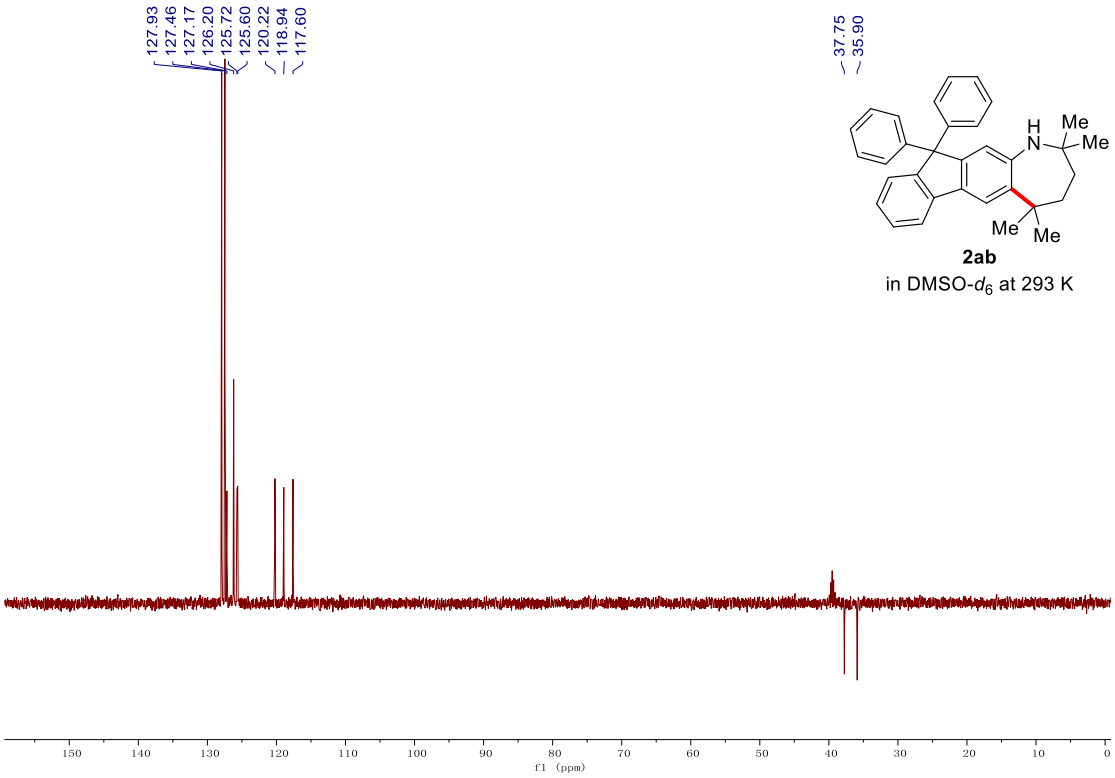
2ab

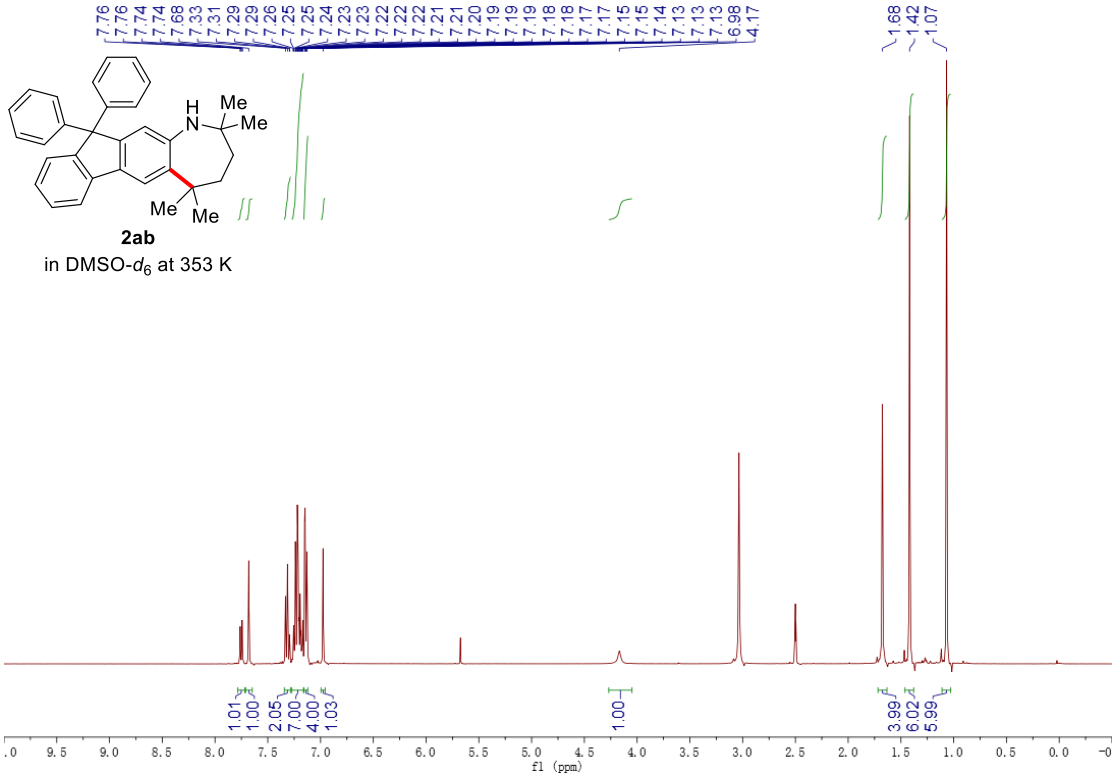
in DMSO-d_6 at 293 K

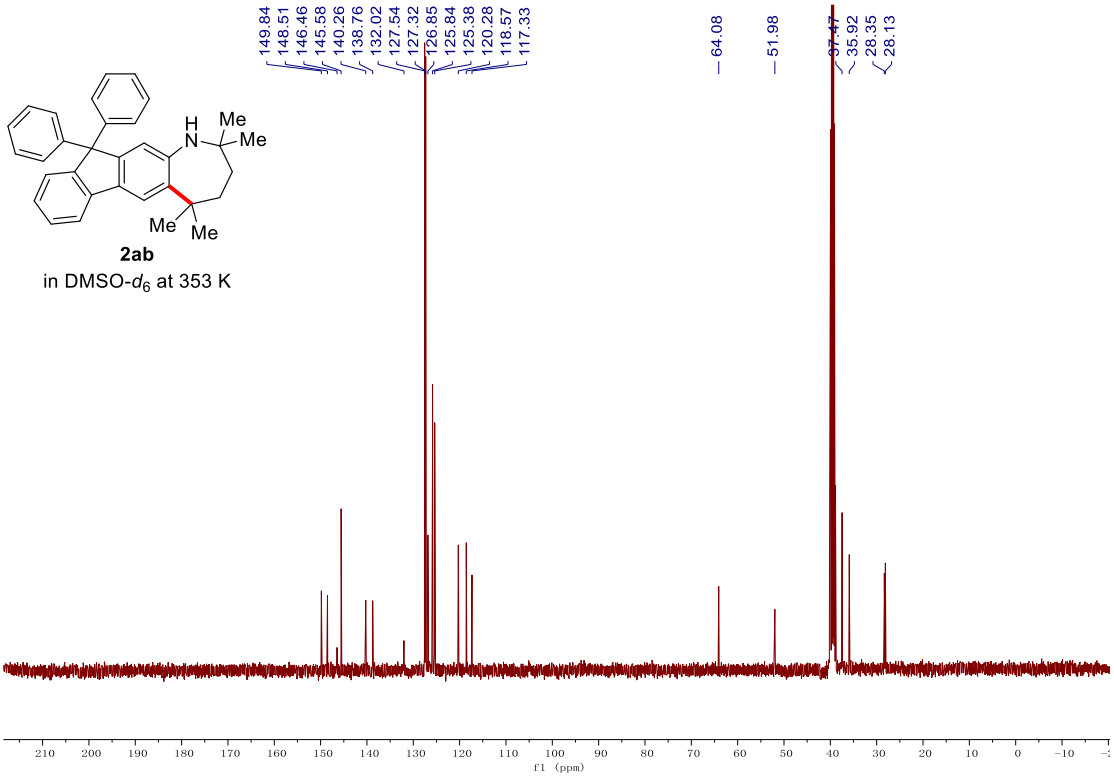


2ab

in DMSO-d_6 at 293 K

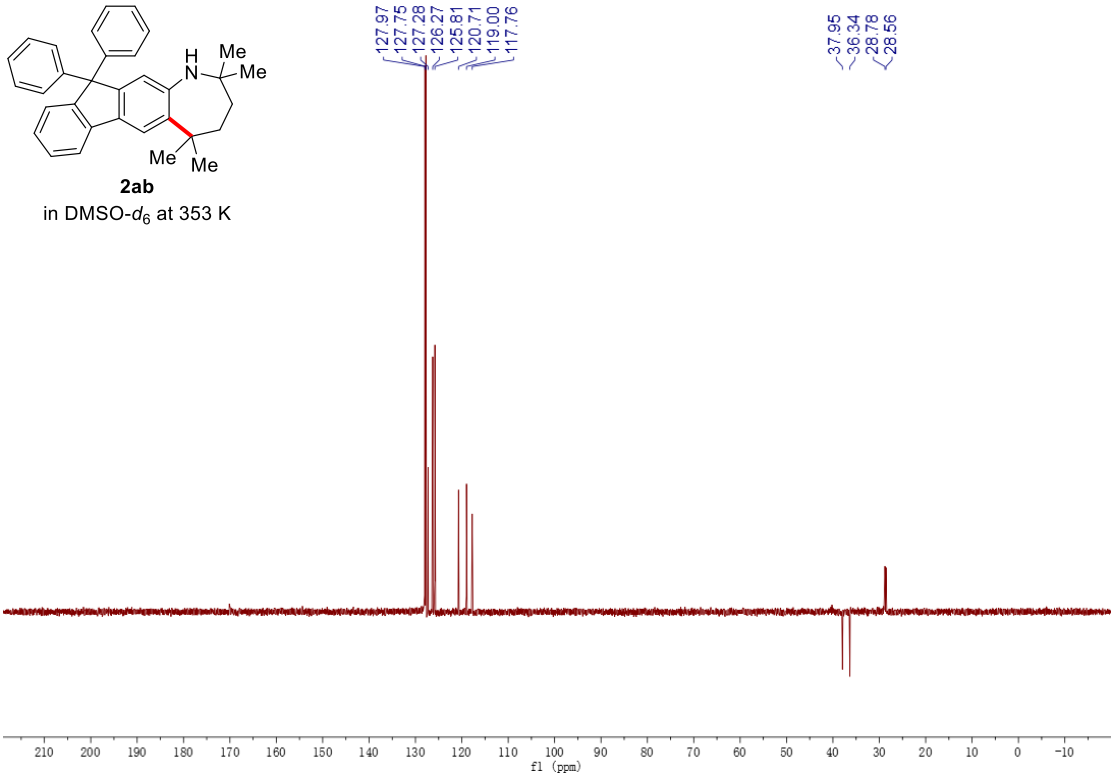

127.93
127.46
127.17
126.20
125.72
125.60
120.22
118.94
117.60
37.75
35.90
H
N
Me
Me
Me
Me
2ab
in DMSO-d_6 at 293 K
f1 (ppm)


7.76
7.76
7.74
7.74
7.68
7.33
7.31
7.29
7.29
7.26
7.25
7.25
7.24
7.23
7.23
7.22
7.22
7.22
7.21
7.21
7.20
7.19
7.19
7.19
7.18
7.18
7.17
7.17
7.15
7.15
7.14
7.13
7.13
7.13
6.98
4.17
1.68
1.42
1.07
H
N
Me
Me
Me
Me
2ab
in DMSO-d_6 at 353 K
1.01
1.00
2.05
7.00
4.00
1.03
1.00
3.99
6.02
5.99
f1 (ppm)



2ab

in DMSO-d_6 at 353 K



2ab

in DMSO-d_6 at 353 K