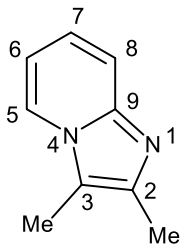
Electronic supplementary materials *Mendeleev Commun.*, 2023, **33**, 164–166

Acetylene-driven multi-molecular assemblies of high complexity: imidazo[1,2-*a*]pyridines and 5-chloro-*N*-[2-(imidazo[1,2-*a*]pyridin-6-yl)vinyl]pyridin-2-amine

Nadezhda V. Semenova, Elena Yu. Schmidt, Igor A. Ushakov and Boris A. Trofimov

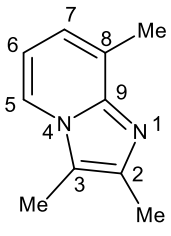
The IR spectra were recorded on a Bruker IFS25 spectrophotometer. The NMR spectra were recorded on a Bruker DPX-400 and AV-400 spectrometers (400.1 MHz for ^{1}H, 100.6 MHz for ^{13}C, and 40.5 MHz for ^{15}N) in $CDCl_3$. The values of the δ ^{15}N were measured through the 2D ^{1}H-^{15}N HMBC experiment and were referenced to CH_3NO_2 (0.0 ppm). Coupling constants (*J*) in hertz (Hz) were measured from one-dimensional spectra and multiplicities were abbreviated as following: s (singlet), d (doublet), dd (doublet of doublet), m (multiplet). Mass spectra of positive electron ionization ions (70 eV) were registered on a Shimadzu GCMS-QP5050A with a DI-50 direct sample injection system (quadrupole mass analyzer, range of detected masses 34 - 650 Da).

2,3-Dimethylimidazo[1,2-a]pyridine **2a** was prepared from **1a** (10 mmol, 0.94 g) and was isolated as a beige powder (0.87 g, 60% yield). M.p. 48-50 ºC.



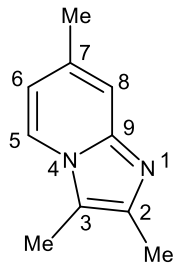
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.79 (d, ^{2}J = 6.8 Hz, 1H, H5), 7.51 (d, ^{2}J = 9.0 Hz, 1H, H8), 7.10 (t, ^{2}J = 7.9 Hz, 1H, H6), 6.78 (t, ^{2}J = 6.8 Hz, 1H, H7), 2.43 (s, 3H, 2-Me), 2.40 (s, 3H, 3-Me). Lit.,[S1] δ: 7.55 (H5), 7.25 (H8), 6.85 (H6), 6.50 (H7), 2.22, 2.19 (2-Me, 3-Me). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 147.2 (C9), 143.6 (C2), 122.5 (C7), 122.5 (C5), 116.6 (C8), 115.4 (C3), 111.6 (C6), 13.2 (2-Me), 8.2 (3-Me). ^{15}N NMR (41 MHz, $CDCl_3$) δ: -178.9 (N4), -144.9 (N1). IR (film, ν/cm^{-1}): 3074, 2966, 2919, 2858, 2357, 1873, 1634, 1573, 1497, 1438, 1404, 1342, 1269, 1245, 1116, 751, 731. Found (%): C, 73.79; H, 6.84; N, 18.91. Calc. for $C_9H_{10}N_2$ (%): C, 73.94; H, 6.89; N, 19.16. MS (EI), *m/z* (%):146.10 $[M]^{+\cdot}$. Calc. for $C_9H_{10}N_2$ *m/z*: 146.08.

2,3,8-Trimethylimidazo[1,2-a]pyridine **2b** was prepared from **1b** (10 mmol, 1.08 g) and was isolated as a beige powder (0.81 g, 50% yield). M.p. 98.0-100.8 ºC.



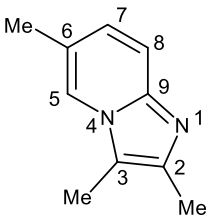
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.66 (d, *J* = 6.7 Hz, 1H, H5), 6.90 (d, *J* = 6.8 Hz, 1H, H7), 6.70 (dd, *J* = 6.7 Hz, *J* = 6.8 Hz, 1H, H6), 2.60 (s, 3H, 8-Me), 2.45 (s, 3H, 2-Me), 2.38 (s, 3H, 3-Me). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 144.4 (C9), 138.8 (C2), 126.4 (C8), 121.8 (C7), 120.4 (C5), 115.9 (C3), 111.5 (C6), 17.1 (8-Me), 13.4 (2-Me), 8.5 (3-Me). ^{15}N NMR (41 MHz, $CDCl_3$) δ: -179.1 (N4), -146.6 (N1). IR (film, ν/cm^{-1}): 3032, 2915, 2360, 1892, 1828, 1772, 1628, 1569, 1491, 1440, 1410, 1347, 1255, 1265, 1107, 881, 770, 749. Found (%): C, 74.88; H, 7.53; N, 17.35. Calc. for $C_{10}H_{12}N_2$ (%): C, 74.97; H, 7.55; N, 17.48. MS (EI), *m/z* (%): 160.15 $[M]^{+\cdot}$. Calc. for $C_{10}H_{12}N_2$ *m/z* 160.1.

2,3,7-Trimethylimidazo[1,2-a]pyridine **2c** was prepared from **1c** (10 mmol, 1.08 g) and was isolated as a beige powder (0.77 g, 48% yield). M.p. 92.1-94.3 ºC.



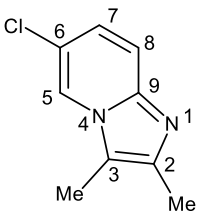
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.61 (d, J = 7.1 Hz, 1H, H5), 7.21 (s, 1H, H8), 6.56 (dd, J = 7.1 Hz, J = 1.3 Hz, 1H, H6), 2.35 (s, 3H, 2-Me), 2.34 (s, 3H, 7-Me), 2.32 (s, 3H, 3-Me). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 144.4 (C9), 139.0 (C2), 133.5 (C7), 121.8 (C5), 115.2 (C8), 114.8 (C3), 114.0 (C6), 21.2 (7-Me), 13.3 (2-Me), 8.3 (3-Me). ^{15}N NMR (41 MHz, $CDCl_3$) δ: -180.7 (N4), -144.4 (N1). IR (film, ν/cm^{-1}): 3058, 2972, 2917, 2859, 2365, 1645, 1611, 1443, 1404, 1348, 1249, 1164, 1122, 1036, 859, 776. Found (%): C, 75.01; H, 7.39; N, 17.43. Calc. for $C_{10}H_{12}N_2$ (%): 74.97; H, 7.55; N, 17.48. MS (EI), *m/z* (%): 160.15 $[M]^{+\cdot}$. Calc. for $C_{10}H_{12}N_2$ *m/z*: 160.10.

2,3,6-Trimethylimidazo[1,2-a]pyridine **2d** was prepared from **1d** (10 mmol, 1.08 g) and was isolated as a beige powder (0.85 g, 53% yield). M.p. 76.0-78.0 ºC.



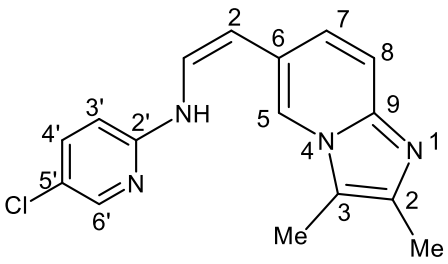
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.55 (s, 1H, H5), 7.40 (d, J = 9.1 Hz, 1H, H8), 6.94 (d, J = 9.1 Hz, 1H, H7), 2.41 (s, 3H, 2-Me), 2.36 (s, 3H, 3-Me), 2.33 (s, 3H, 6-Me). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 143.1 (C9), 139.4 (C2), 125.7 (C7), 121.0 (C6), 120.4 (C5), 116.0 (C8), 115.2 (C3), 18.4 (6-Me), 13.3 (2-Me), 8.4 (3-Me). ^{15}N NMR (41 MHz, $CDCl_3$) δ: -178.3 (N4), -143.1 (N1) . IR (film, ν/cm^{-1}): 3068, 3042, 2968, 2919, 2857, 2360, 1921, 1641, 1620, 1572, 1535, 1508, 1455, 1440, 1400, 1335, 1274, 1257, 1208, 1129, 1038, 800, 638. Found (%): C, 75.05; H, 7.48; N, 17.11. Calc. for $C_{10}H_{12}N_2$ (%): 74.97; H, 7.55; N, 17.48. MS (EI), *m/z* (%):160.15 $[M]^{+\cdot}$. Calc. for $C_{10}H_{12}N_2$ *m/z*: 160.1.

6-Chloro-2,3-dimethylimidazo[1,2-a]pyridine **2e** was prepared from **1e** (10 mmol, 1.28 g) and was isolated as a beige powder (0.36 g, 20% yield). M.p. 129.0-134.0 ºC.



^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.81 (s, 1H, H5), 7.43 (d, J = 9.4 Hz, 1H, H8), 7.05 (dd, J = 9.5 Hz, J = 2.0 Hz, 1H, H7), 2.41 (s, 3H, 2-Me), 2.38 (s, 3H, 3-Me). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 142.3 (C9), 141.0 (C2), 123.9 (C7), 120.5 (C6), 119.8 (C5), 117.0 (C8), 116.4 (C3), 13.4 (2-Me), 8.4 (3-Me) . IR (film, ν/cm^{-1}): 3034, 2919, 2857, 2360, 1922, 1616, 1566, 1516, 1496, 1443, 1404, 1321, 1245, 1162, 1136, 1083, 1047, 920, 806. Found (%): C, 59.86; H, 5.20; Cl, 19.35; N, 15.30. Calc. for $C_9H_9ClN_2$ (%): C, 59.84; H, 5.02; Cl, 19.63; N, 15.51. MS (EI), *m/z* (%):180.10 $[M]^{+\cdot}$. Calc. for $C_9H_9ClN_2$ *m/z*: 180.05.

(Z)-5-Chloro-N-(2-(2,3-dimethylimidazo[1,2-a]pyridin-6-yl)vinyl)pyridin-2-amine **3e** was prepared from **1e** (10 mmol, 1.28 g) and was isolated as a beige powder (0.61 g, 40% yield). M.p. 228.2-232.6 °C.

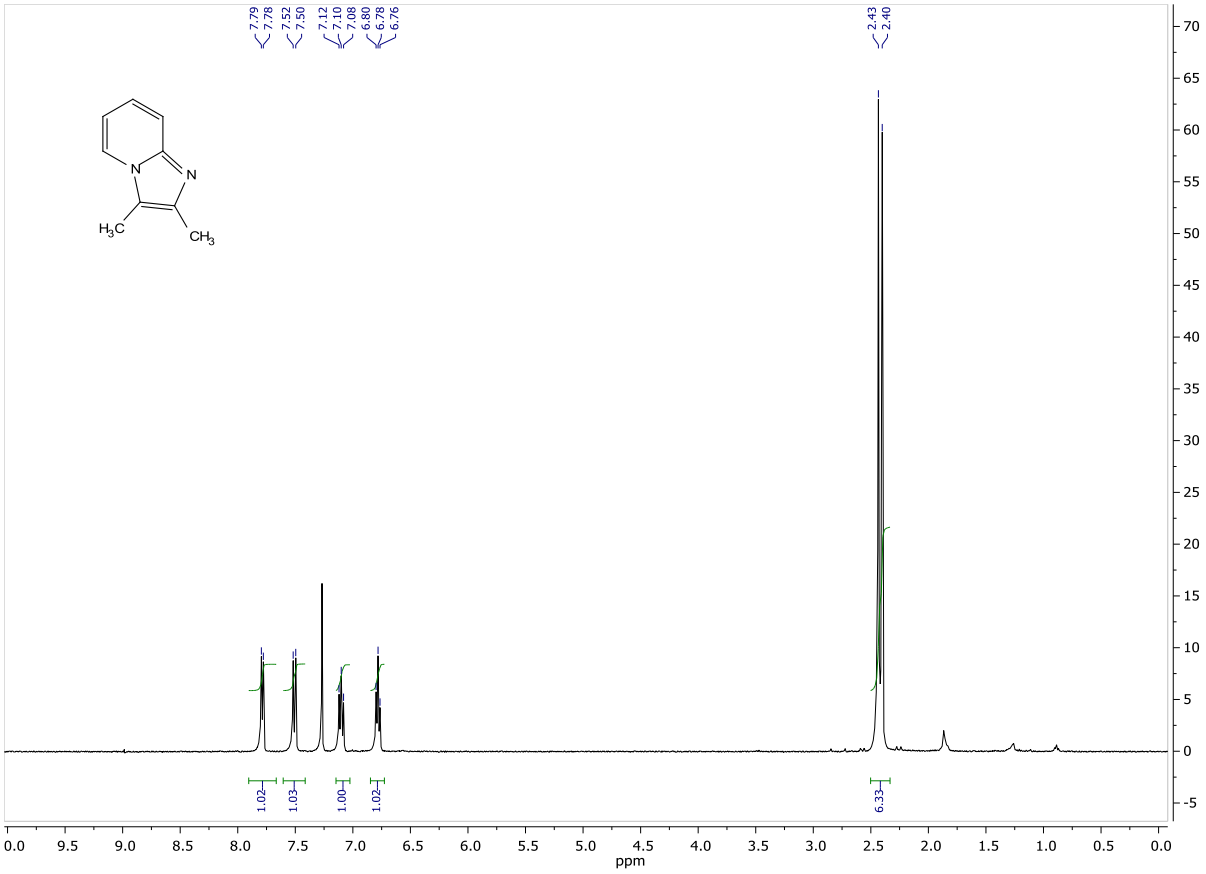


^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.94 (d, J = 10.5 Hz, 1H, NH), 8.16 (d, J = 2.6 Hz, 1H, H6'), 7.71 (dd, J = 13.5 Hz, J = 10.5 Hz, 1H, NH-C<u>H</u>=), 7.67-7.65 (m, 1H, H4'), 7.18-7.15 (m, 1H, H8), 7.03-6.99 (m, 1H, H7), 6.83-6.81 (m, 1H, H3'), 6.77 (d, J = 13.5 Hz, 1H, =CH), 6.74-6.72 (m, 1H, H5), 2.68 (s, 3H, 3-Me), 2.25 (s, 3H, 2-Me). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 152.3 (C2'), 145.9 (C6'), 144.7 (C9), 139.8 (C2), 137.9 (C6), 137.6 (C4'), 129.3 (NH-C<u>H</u>=), 123.3 (C7), 121.0 (C5'), 116.7 (C3), 113.1 (C8), 110.7 (C3'), 108.1 (C5), 99.7 (=CH), 13.3 (3-Me), 12.9 (2-Me). IR (film, ν/cm^{-1}): 3052, 2955, 2922, 2856, 1902, 1652, 1598, 1571, 1477, 1368, 1290, 1225, 1125, 1107, 962, 821, 803, 777, 737, 723. Found (%): C, 64.28; H, 5.16; Cl, 11.66; N, 18.58. Calc. for $C_{16}H_{15}ClN_4$ (%): C, 64.32; H, 5.06; Cl, 11.87; N, 18.75. MS (EI), *m/z* (%):298.20 $[M]^{+\cdot}$. Calc. for $C_{16}H_{15}ClN_4$ *m/z*: 298.10.

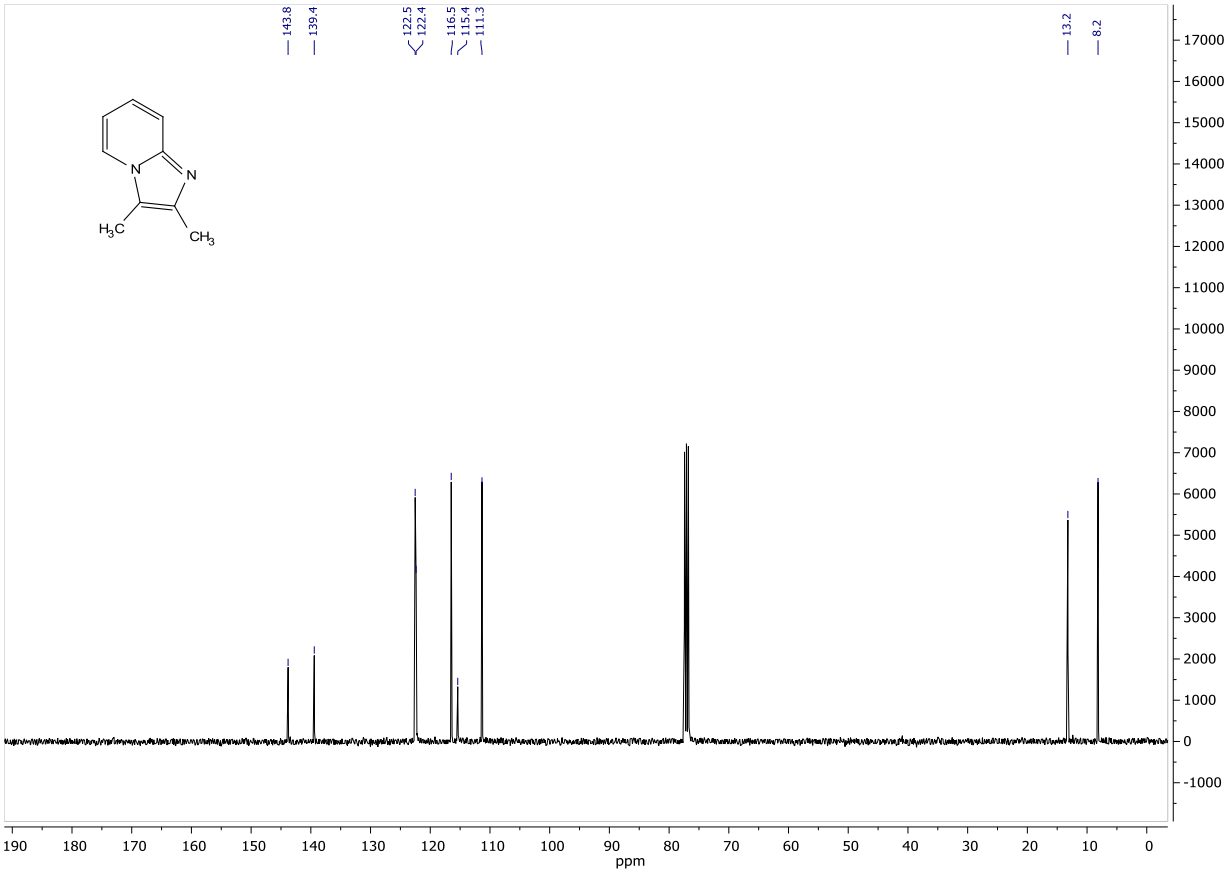
References

S1 M. A. Andriyankov, G .G. Skvorzova and V. K. Voronov, *Zh. Org. Khim*., 1983, **19**, 2459 (in Russian).

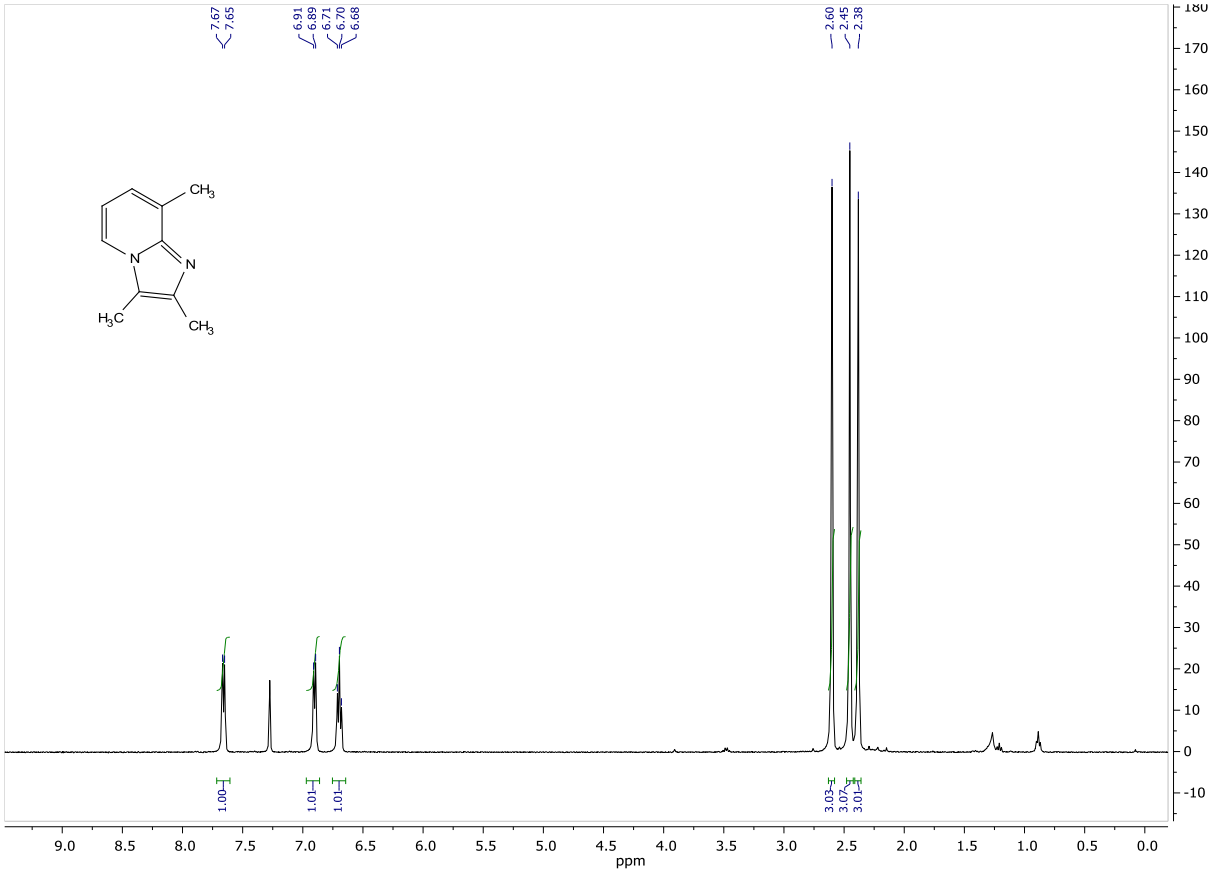
NMR Spectra



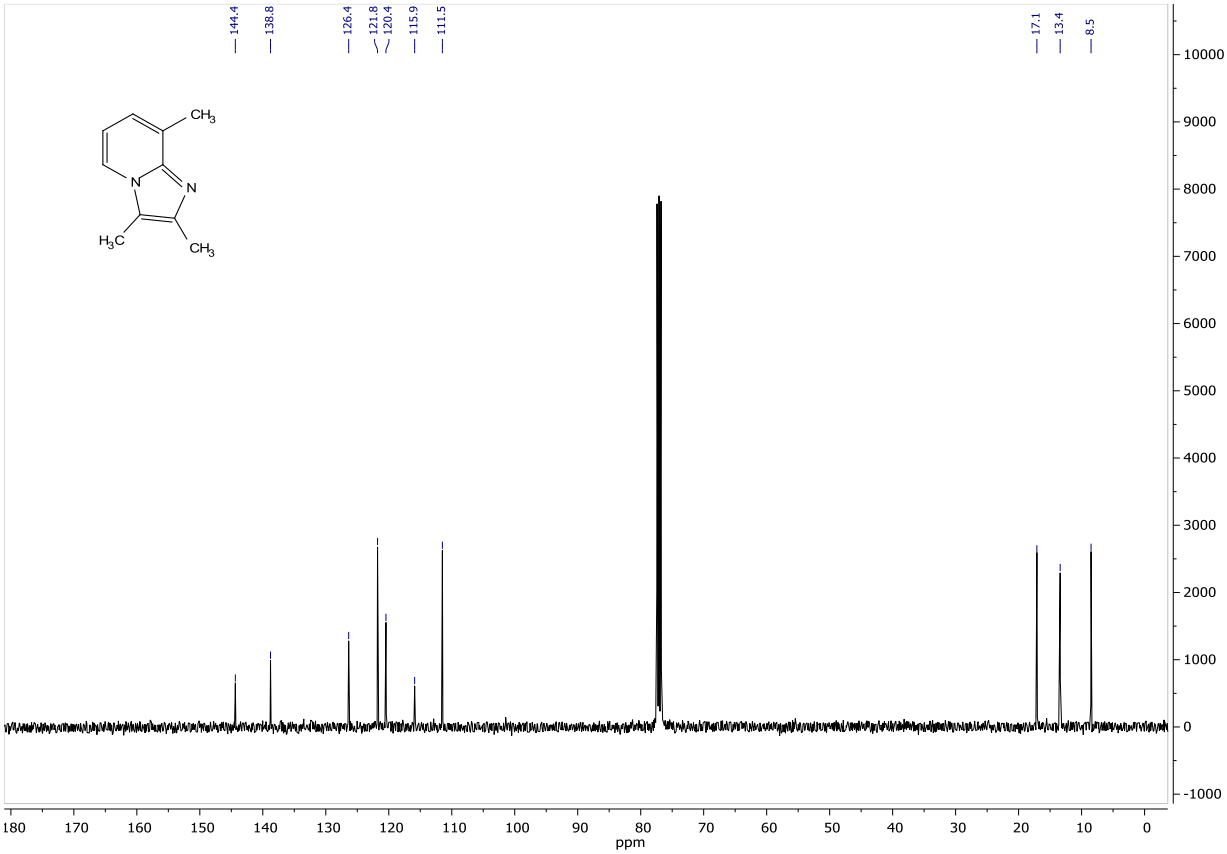
^{1}H NMR Spectrum of **2a** (400.1 MHz, $CDCl_3$)



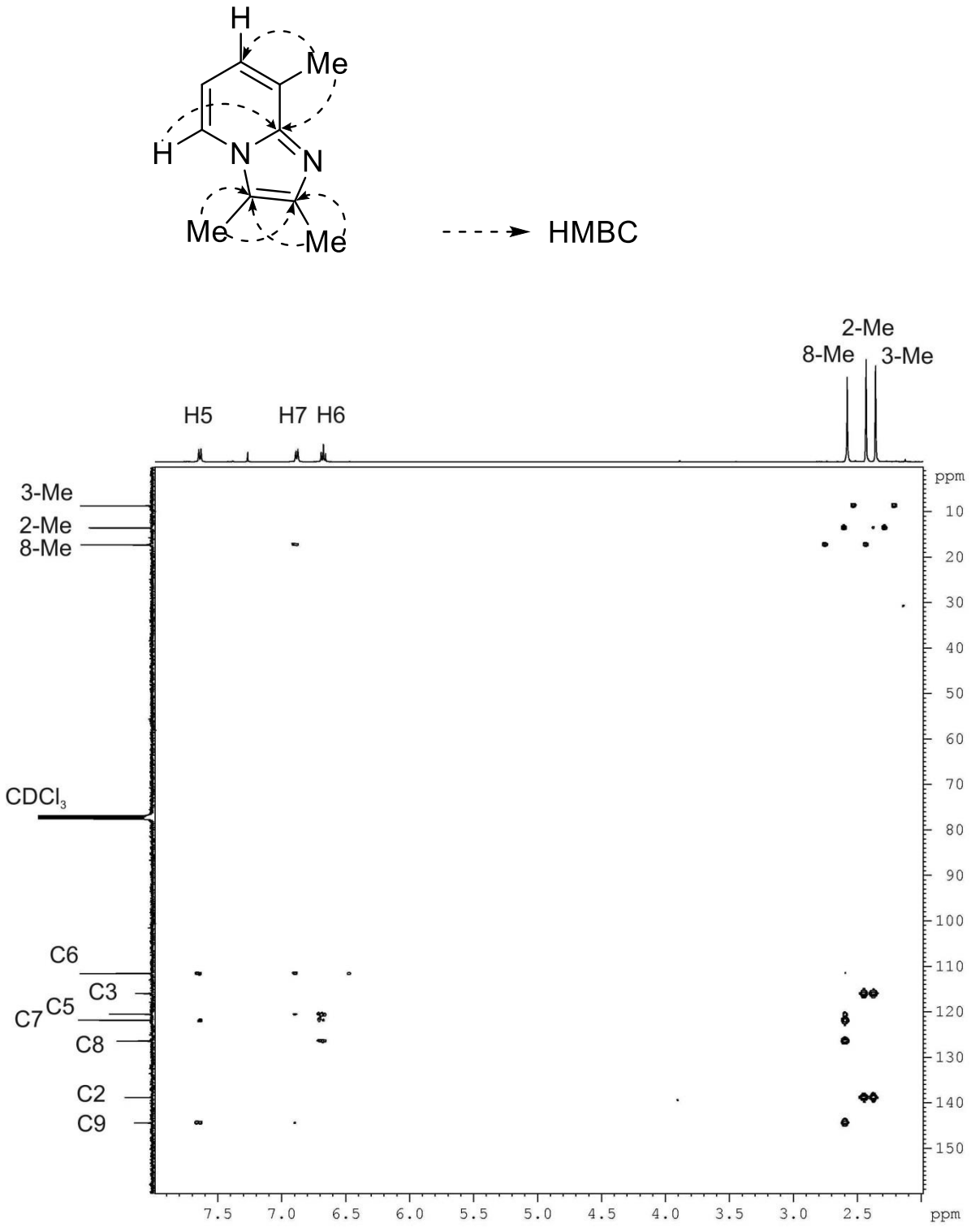
^{13}C NMR Spectrum of **2a** (100.6 MHz, $CDCl_3$)



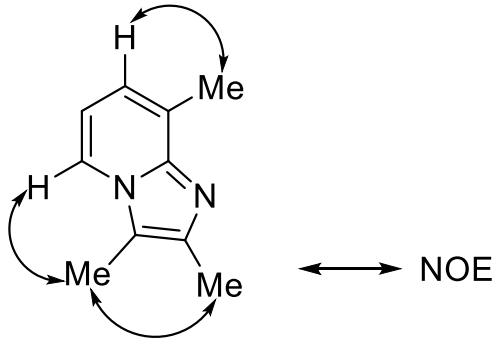
^{1}H NMR Spectrum of **2b** (400.1 MHz, $CDCl_3$)

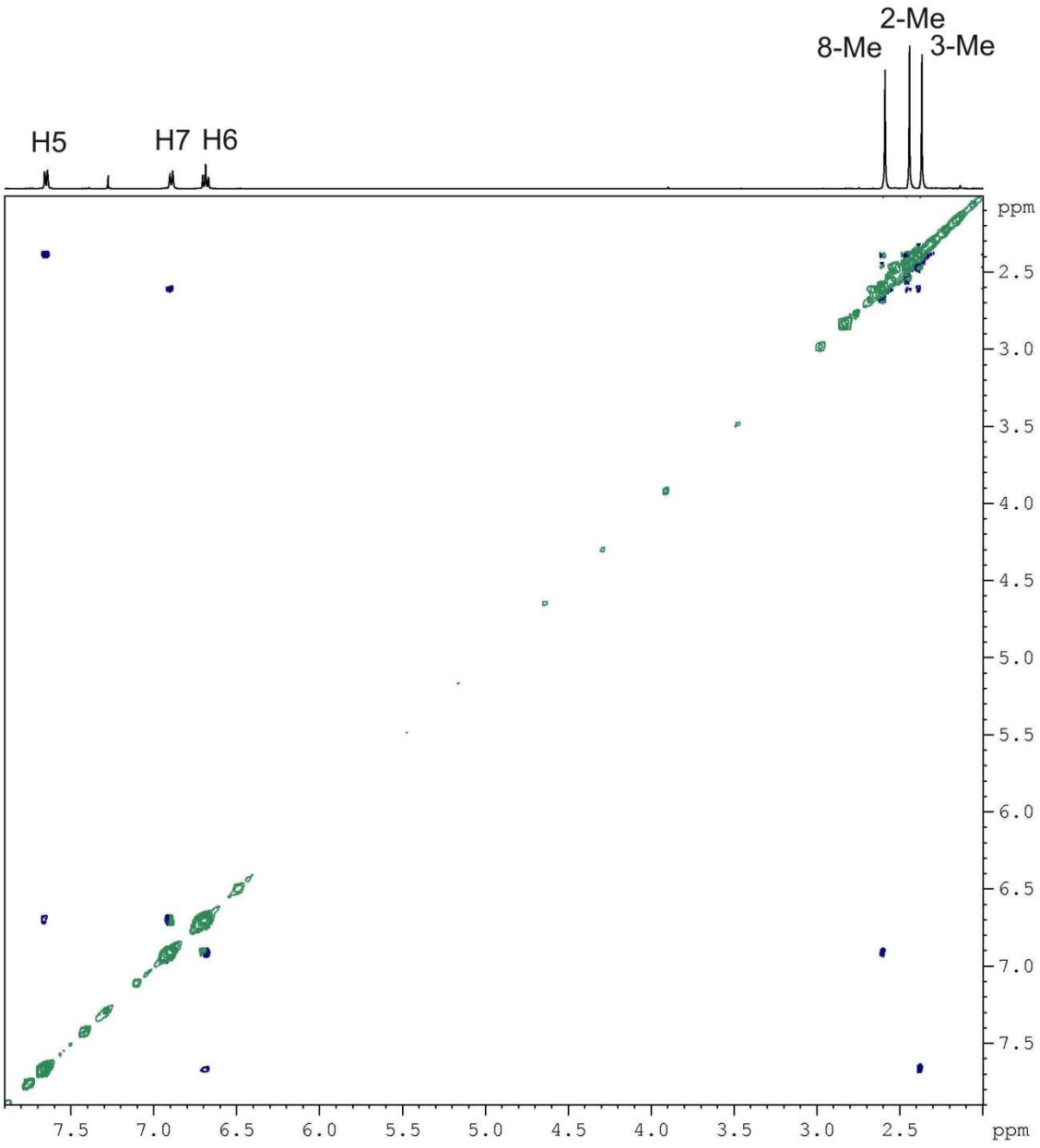


^{13}C NMR Spectrum of **2b** (100.6 MHz, $CDCl_3$)

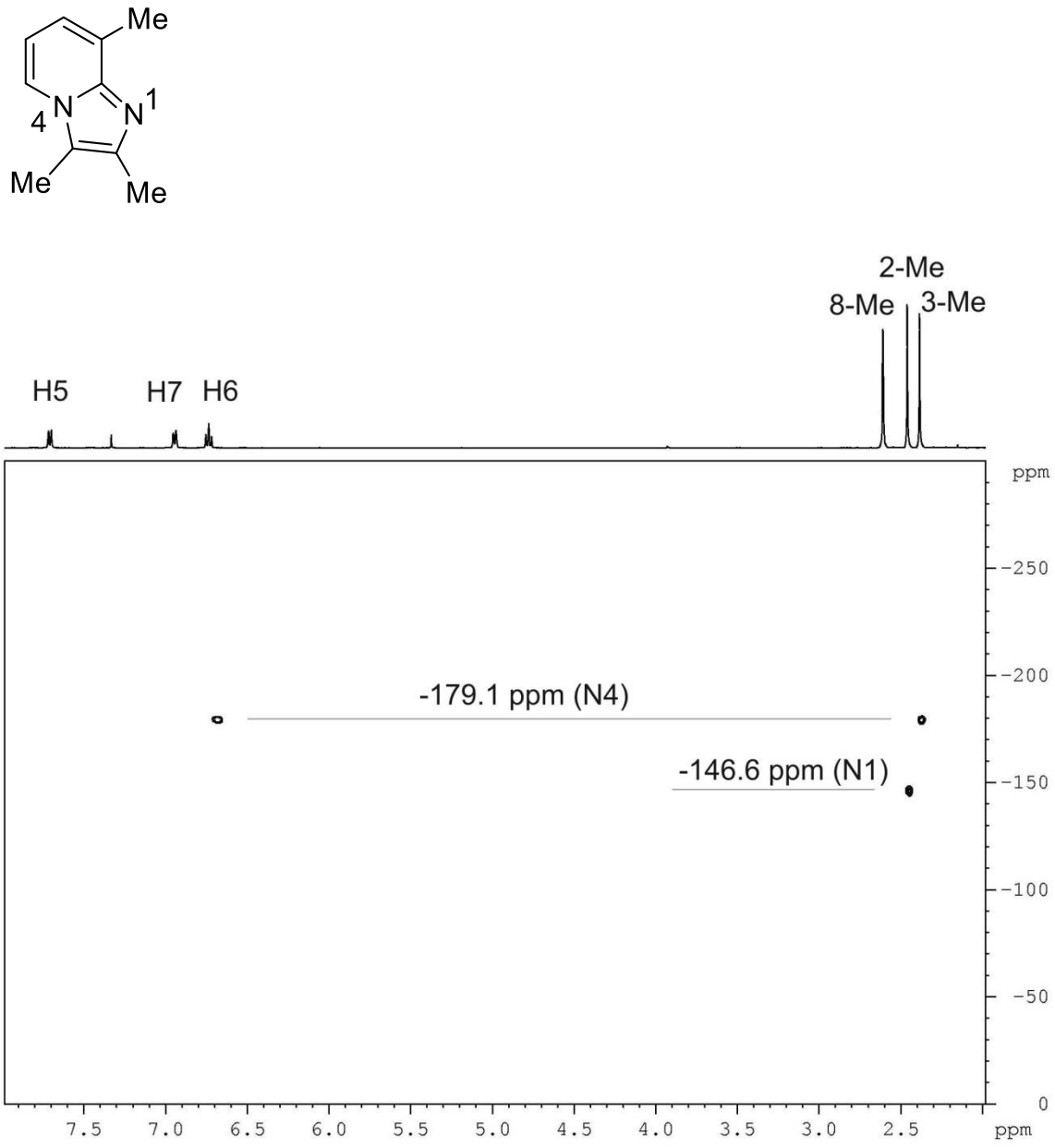


2D ^{1}H-^{13}C HMBC spectrum of **2b** ($CDCl_3$)

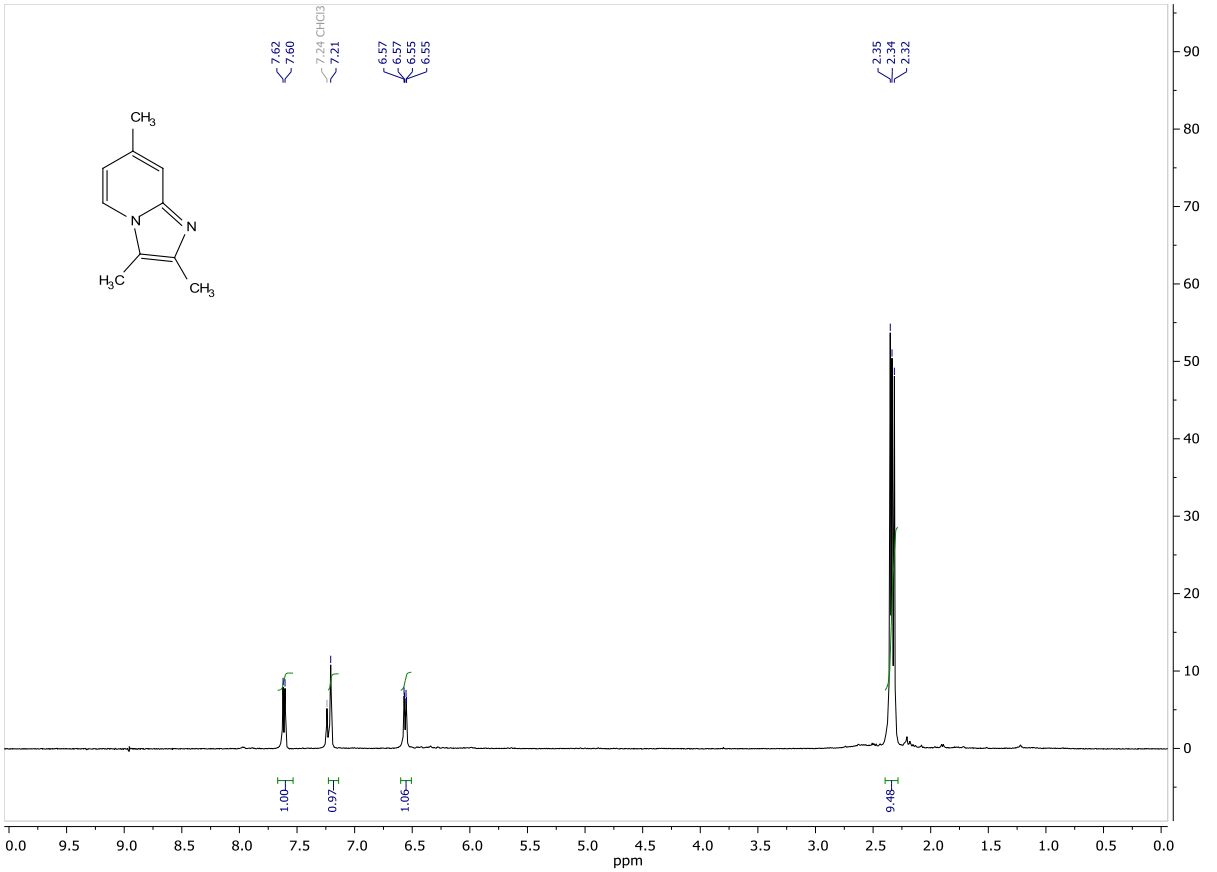




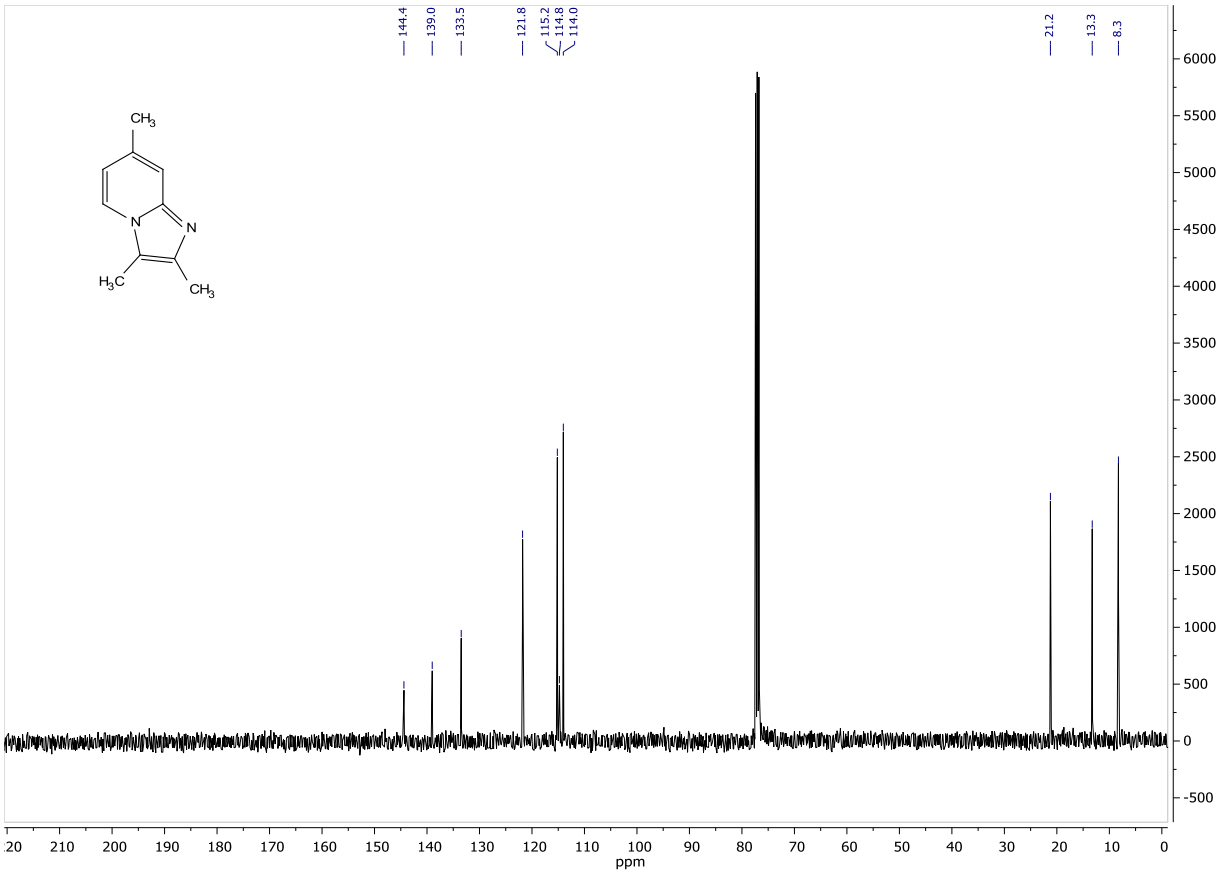
2D NOESY spectrum of **2b** ($CDCl_3$)



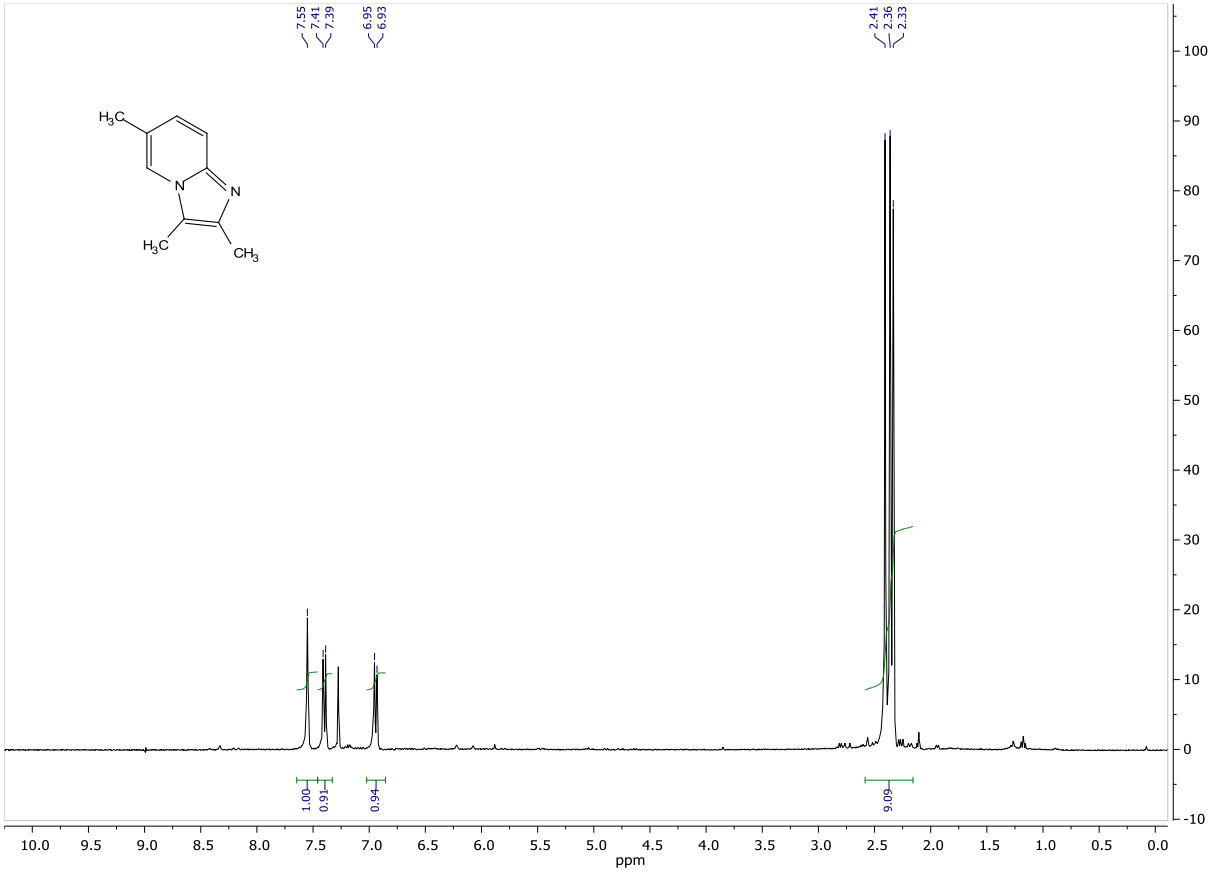
2D ^{1}H-^{15}N HMBC spectrum of **2b** ($CDCl_3$)



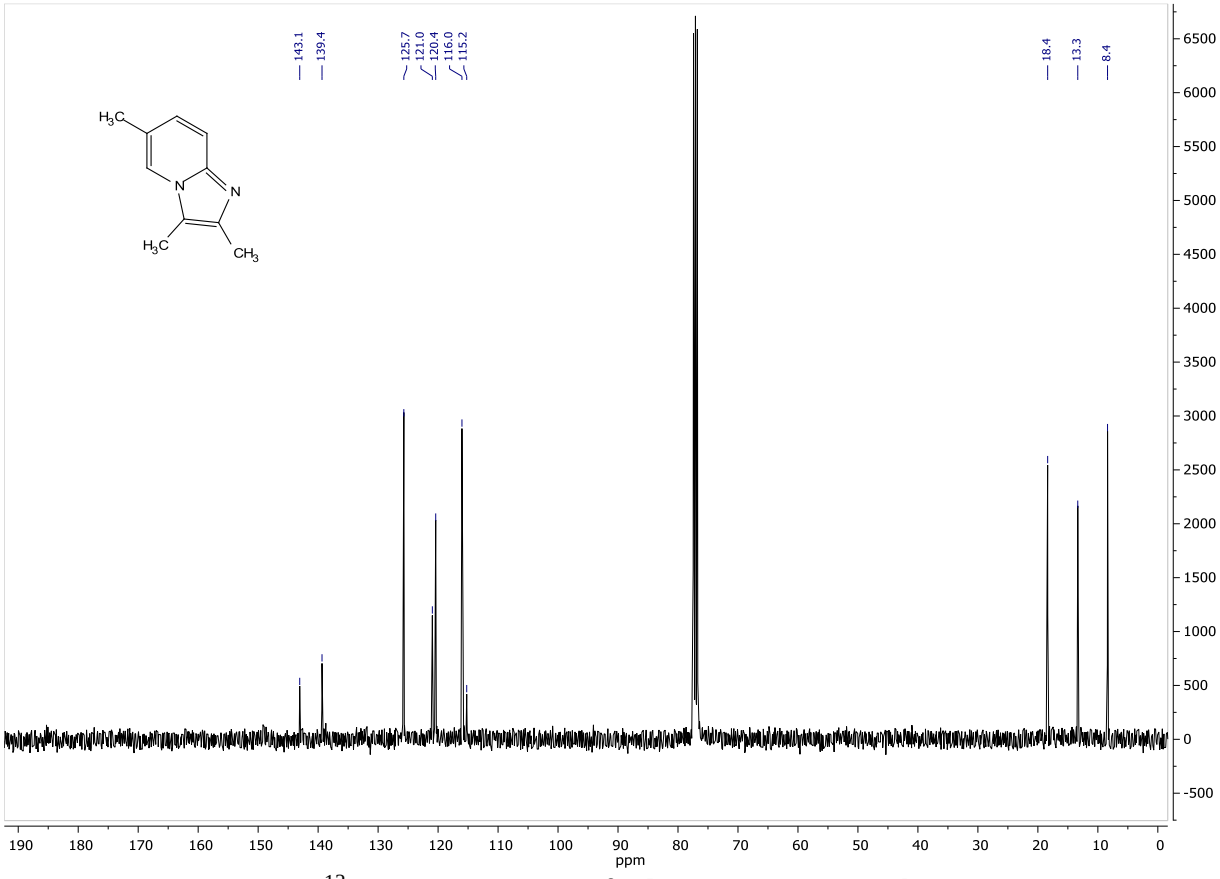
^{1}H NMR spectrum of **2c** (400.1 MHz, $CDCl_3$)



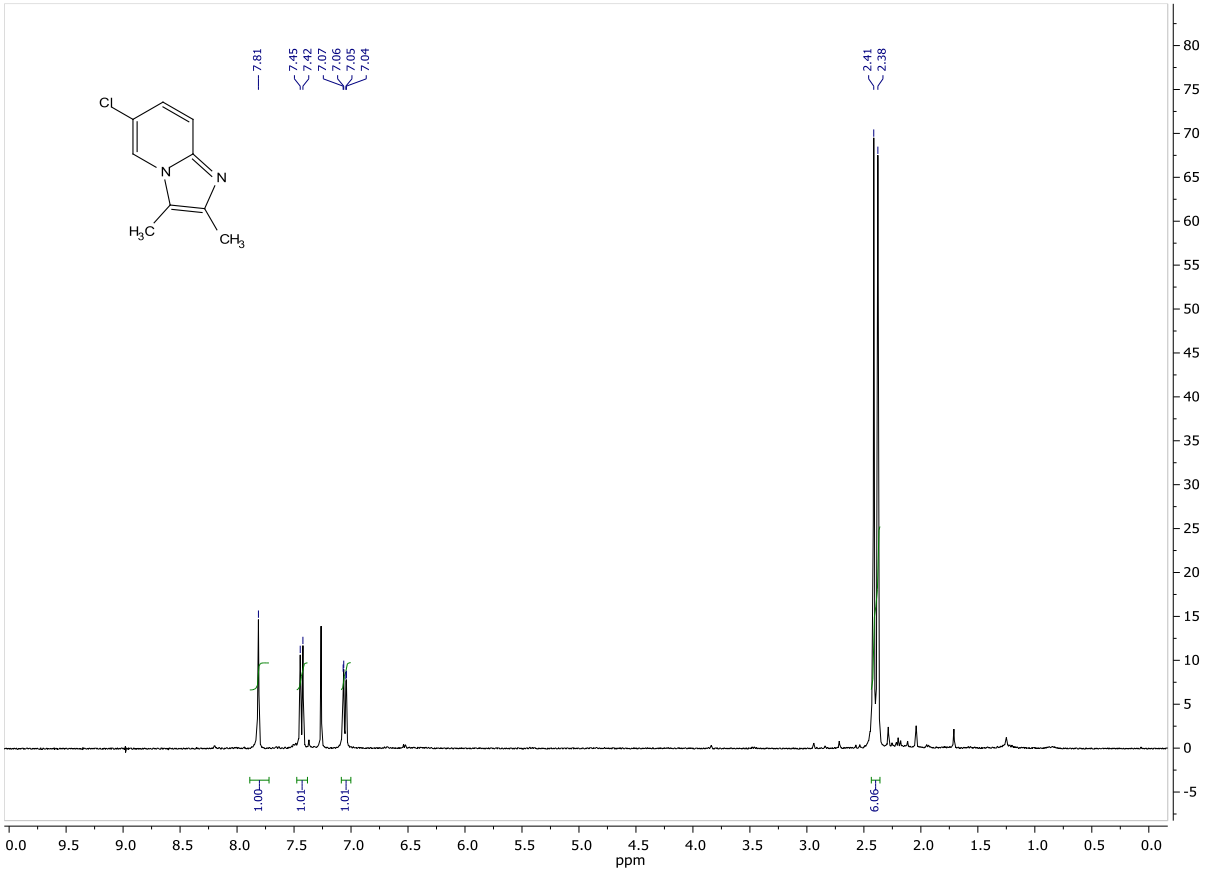
^{13}C NMR spectrum of **2c** (100.6 MHz, $CDCl_3$)



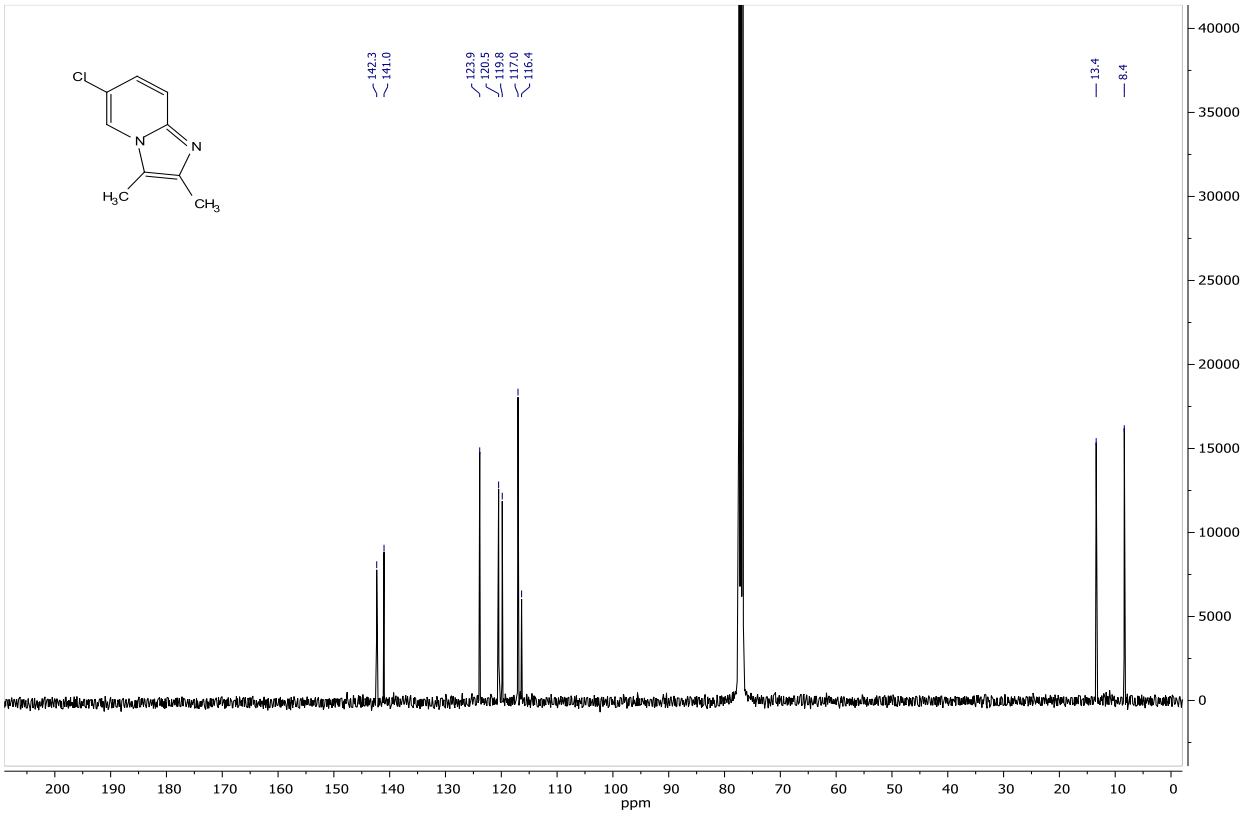
^{1}H NMR spectrum of **2d** (400.1 MHz, $CDCl_3$)



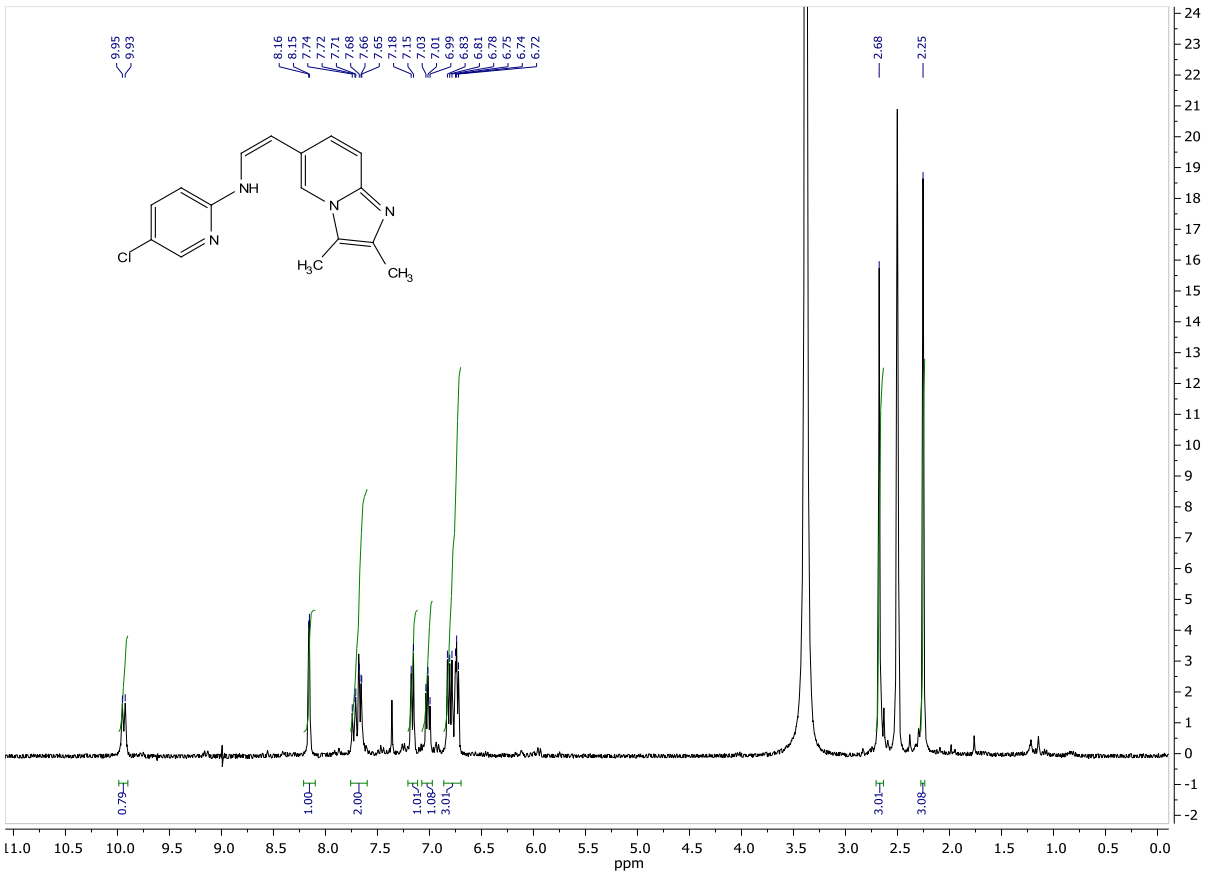
^{13}C NMR Spectrum of **2d** (100.6 MHz, $CDCl_3$)



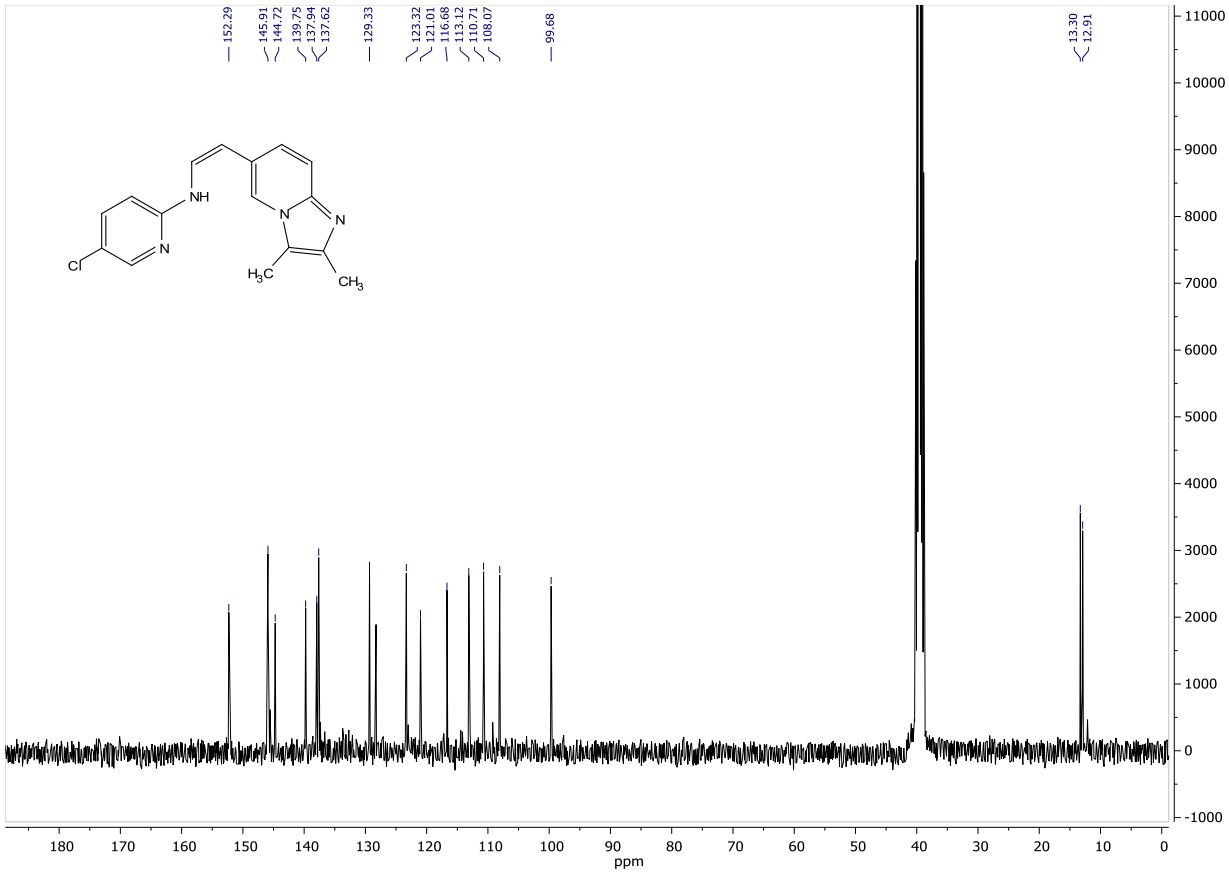
^{1}H NMR spectrum of **2e** (400.1 MHz, $CDCl_3$)



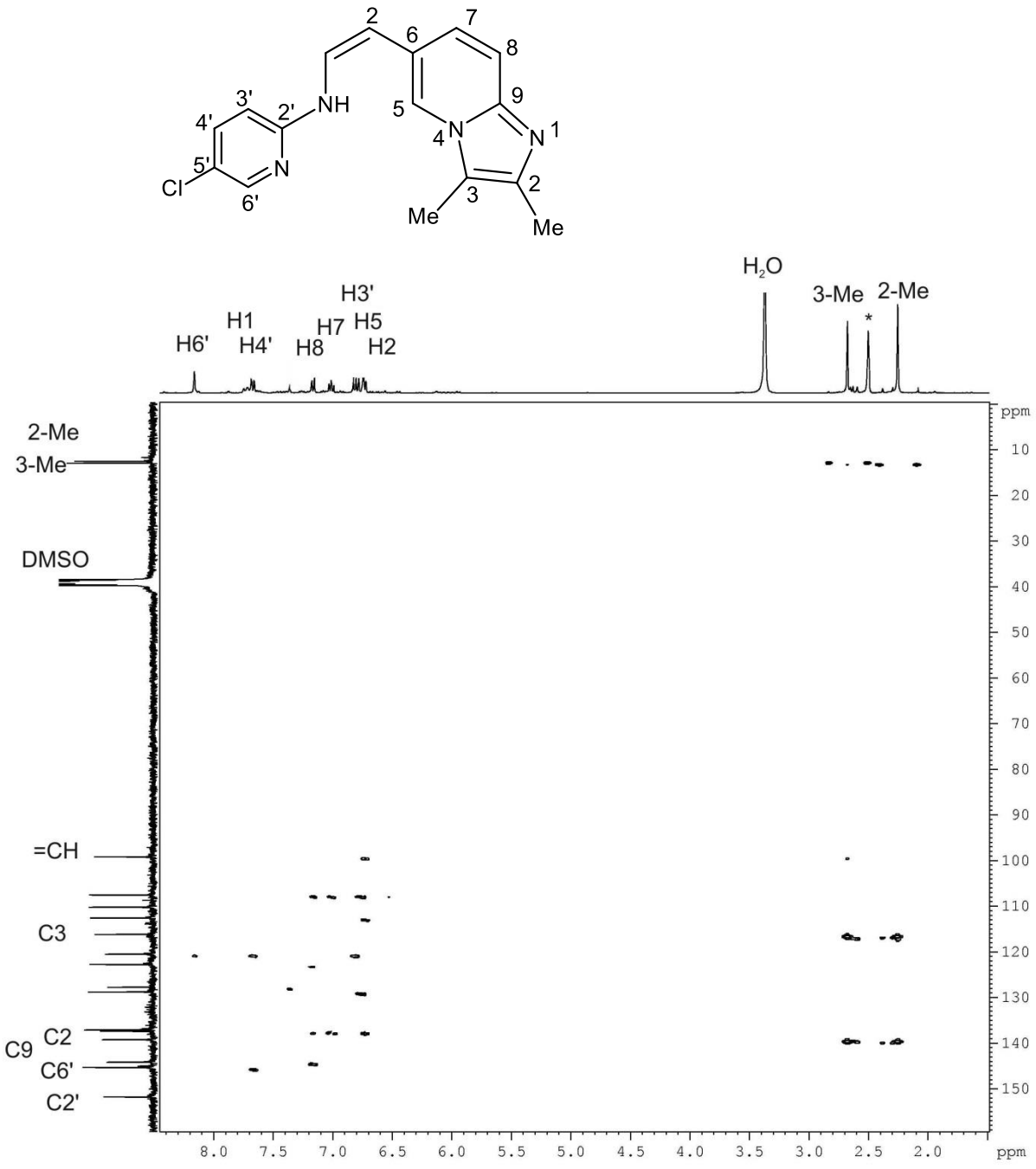
^{13}C NMR spectrum of **2e** (100.6 MHz, $CDCl_3$)



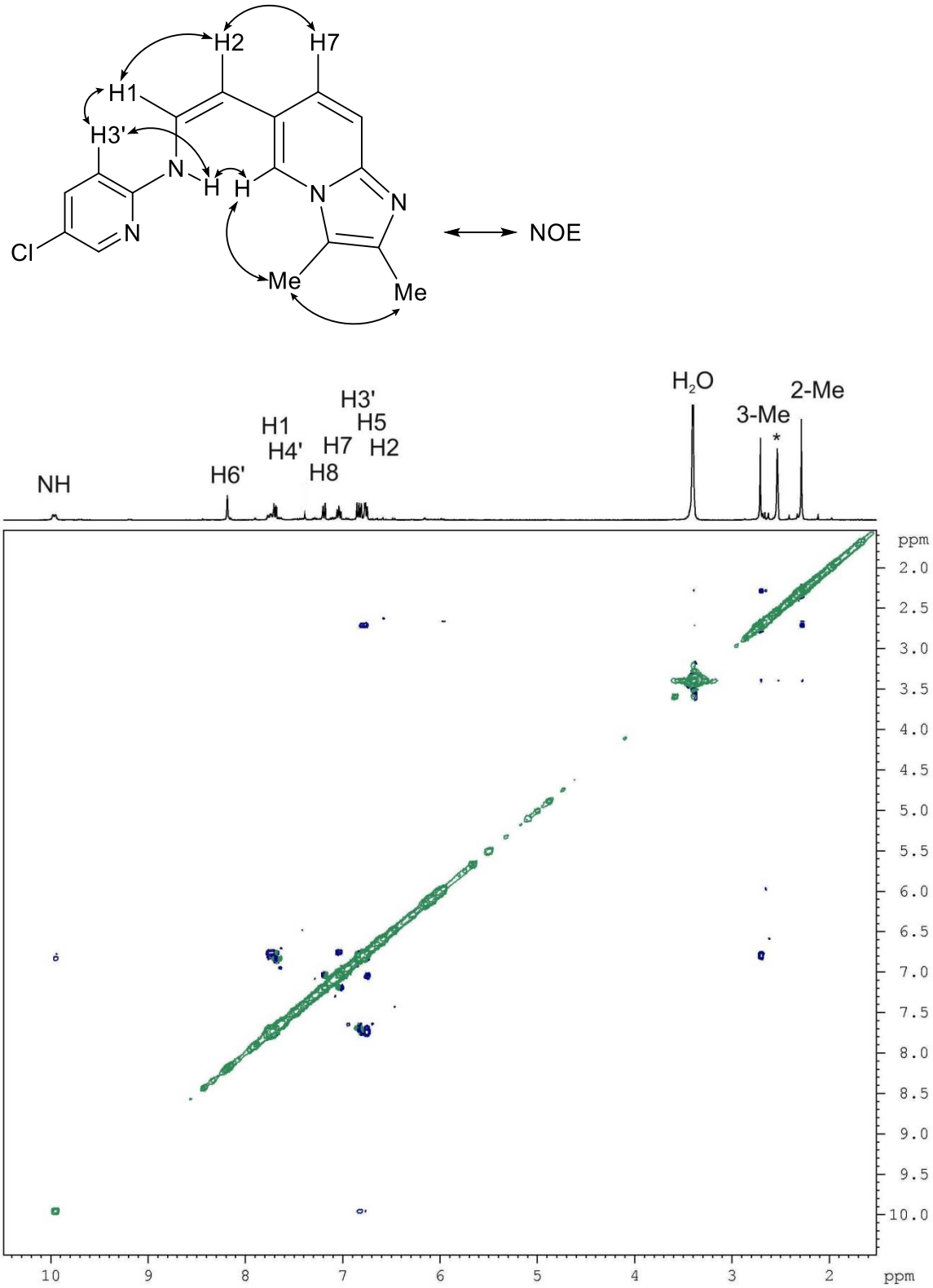
^{1}H NMR spectrum of **3e** (400.1 MHz, DMSO)



^{13}C NMR spectrum of **3e** (100.6 MHz, DMSO)



2D ^{1}H-^{13}C HMBC spectrum of **3e** (DMSO-d_6)



2D NOESY spectrum of **3e** (DMSO-d_6)