Rh^{III}-catalyzed formal C–H [5+1] cyclization of 2-pyrrolyl/indolylanilines using vinylene carbonate as a C1 synthon

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Supporting Information

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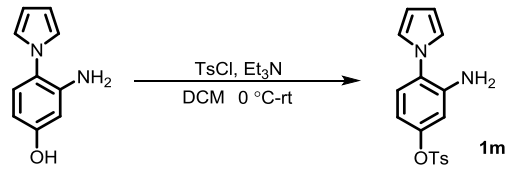
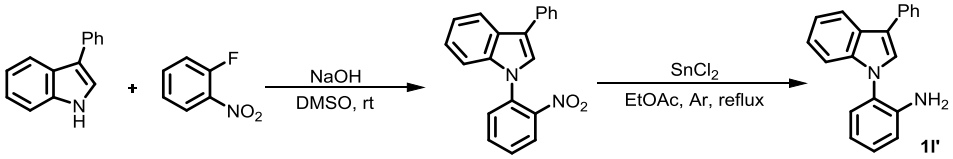
A. General information:

All reagents were used as received unless otherwise noted. Analytical thin-layer chromatography was performed with 0.25 mm coated commercial silica gel plates (TLC Silica Gel 60 F_{254}); visualization of the developed chromatogram was performed by fluorescence. Flash Chromatography was performed with silica gel (300-400 mesh). Proton-1 nuclear magnetic resonance (^{1}H NMR) data were acquired at 400 MHz on a Bruker Ascend 400 (400 MHz) spectrometer, and chemical shifts are reported in delta (δ) units, in parts per million (ppm) downfield from tetramethylsilane. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet, coupling constants *J* are quoted in Hz. Carbon-13 nuclear magnetic resonance (^{13}C NMR) data were acquired at 100 MHz on a Bruker Ascend 400 spectrometer, chemical shifts are reported in ppm relative to the center line of a triplet at 77.0 ppm for $CDCl_3$. Infrared spectra (IR) data were recorded on a TENSOR 27 FT-IR spectrometer and recorded in wave numbers (cm^{-1}). High resolution mass spectra were acquired on a Bruker Daltonics MicroTof-Q II mass spectrometer. **1a-d**[1], **1e**[2], **1f-j**[3], **1k**[4], **1l**[5], **1n-r**[6], **1s**[7], **1t**[3], **1u**[8], **1v**[9], **1w**[10], **1a'**[11], **1b'**[7], **1c'**[5], **1d'**[7], **1e'-1g'**[5], **1h'**[11], **1i'**[5], **1j'**[12], **1k'**[11], **1m'**[13], **1n'**[14] were prepared according to literature methods.

B. Preparation of substrates:



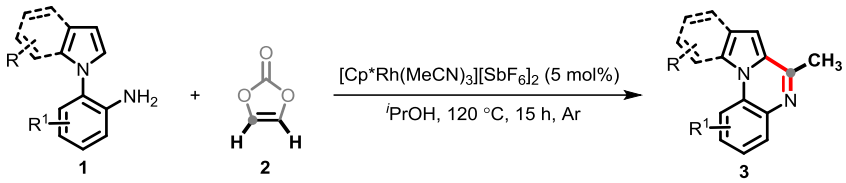
To a stirred solution of 3-amino-4-(1*H*-pyrrol-1-yl)phenol (0.6 mmol) in DCM (3.0 mL) at 0 ℃ were added Et_3N (0.72 mmol) and TsCl (0.66 mmol) slowly. After stirring at 0 ℃ for 4 h, the reaction mixture was extracted with $CHCl_3$ and washed with brine. The organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was then chromatographed on silica gel to afford the product **1m**. Pale yellow solid (153.5 mg, 78% yield). PE/EA = 5:1, R_f = 0.31. mp 114-115 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, *J* = 8.3 Hz, 2H), 7.39 (d, *J* = 8.2 Hz, 2H), 7.05 (d, *J* = 8.5 Hz, 1H), 6.84-6.77 (m, 2H), 6.58 (d, *J* = 2.5 Hz, 1H), 6.39-6.32 (m, 3H), 3.84 (s, 2H), 2.51 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.5, 145.4, 143.3, 132.7, 129.8, 128.5, 127.9, 126.1, 121.6, 111.5, 109.8, 109.6, 21.7. IR (KBr): 3477, 3380, 1624, 1503, 1368, 1184, 1138, 967, 818, 734 cm^{-1}. HRMS (ESI) m/z calculated for $C_{17}H_{17}N_2O_3S$ $[M+H]^+$ 329.0954, found 329.0963.



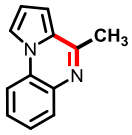
To a stirred solution of 3-phenyl-1*H*-indole (1.0 mmol) and 1-fluoro-2-nitrobenzene (1.0 mmol) in DMSO (1.0 mL), NaOH (1.0 mmol) was added portion wise and is stirred vigorously at room temperature for 1.5 h. After completion of the reaction, the mixture was diluted by H_2O, and extracted by EtOAc. The combined organic layer was washed with brine and dried by anhydrous $MgSO_4$. The solution was evaporated and used for the next step without purification. The crude product in EtOAc (5.0 mL) was added SnCl $2H_2O$ (5.0 mmol) at room temperature, and the resulting reaction mixture was stirred for 18 h. The reaction was quenched by NaOH and extracted by EtOAc. The organic layer was dried by anhydrous $MgSO_4$, evaporated. The residue was then

chromatographed on silica gel to afford the product **1l'**. Pale yellow solid (179.0 mg, 63% yield). PE/EA = 10:1, R_f = 0.37. mp 49-50 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (q, *J* = 4.6, 3.8 Hz, 1H), 7.78 (d, *J* = 7.5 Hz, 2H), 7.53 (t, *J* = 7.7 Hz, 2H), 7.47 (s, 1H), 7.40-7.34 (m, 1H), 7.34-7.28 (m, 4H), 7.26 (dt, *J* = 5.9, 3.0 Hz, 1H), 6.94 (dd, *J* = 12.2, 7.7 Hz, 2H), 3.70 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.2, 137.3, 135.2, 129.4, 128.9, 128.7, 127.5, 126.4, 126.2, 126.2, 124.6, 122.7, 120.7, 120.1, 118.8, 118.6, 116.4, 111.2. IR (KBr): 3470, 3376, 3046, 1613, 1504, 1458, 1310, 1217, 748 cm^{-1}. HRMS (ESI) m/z calculated for $C_{20}H_{17}N_2$ $[M+H]^+$ 285.1386, found 285.1393.

C. Reaction results:



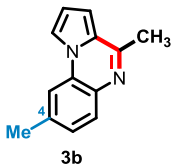
A pressure tube was charged with $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (5 mol%), 2-(1*H*-pyrrol-1-yl)aniline **1** (0.24 mmol), vinylene carbonate **2** (0.2 mmol) and ^{i}PrOH (1.0 mL). The reaction mixture was stirred at 120 ℃ for 15 h under Ar condition. After cooling to room temperature, the mixture was filtered through a short Celite pad and all volatiles were removed under reduced pressure. The residue was purified by silica gel chromatography to afford the product **3**.



3a

4-Methylpyrrolo[1,2-*a*]quinoxaline (3a)

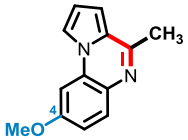
Pale yellow solid (32.4 mg, 89% yield). PE/EA = 10:1, R_f = 0.31. mp 106-107 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98-7.91 (m, 2H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.49 (dt, *J* = 19.3, 7.1 Hz, 2H), 6.98-6.84 (m, 2H), 2.78 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.6, 135.9, 129.3, 127.3, 126.9, 126.3, 125.1, 114.2, 113.6, 113.5, 106.5, 22.0. IR (KBr): 3104, 2917, 1610, 1532, 1480, 1420, 1366, 1215, 1036, 723 cm^{-1}. HRMS (ESI) m/z calculated for $C_{12}H_{11}N_2$ $[M+H]^+$ 183.0917, found 183.0922.



3b

4,8-Dimethylpyrrolo[1,2-*a*]quinoxaline (3b)

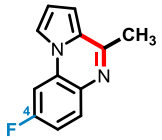
Pale yellow solid (36.9 mg, 94% yield). PE/EA = 20:1, R_f = 0.26. mp 107-108 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (s, 1H), 7.81 (d, *J* = 8.2 Hz, 1H), 7.61 (s, 1H), 7.28-7.22 (m, 1H), 6.90-6.82 (m, 2H), 2.74 (s, 3H), 2.55 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.5, 137.2, 133.9, 129.0, 127.0, 126.4, 126.3, 113.9, 113.7, 113.3, 106.1, 21.9, 21.7. IR (KBr): 3107, 2912, 1619, 1533, 1469, 1418, 1352, 1036, 813, 733 cm^{-1}. HRMS (ESI) m/z calculated for $C_{13}H_{13}N_2$ $[M+H]^+$ 197.1073, found 197.1079.



3c

8-Methoxy-4-methylpyrrolo[1,2-*a*]quinoxaline (3c)

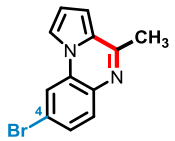
White solid (39.0 mg, 92% yield). PE/EA = 10:1, R_f = 0.32. mp 88-89 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 8.9 Hz, 1H), 7.81 (s, 1H), 7.24 (d, *J* = 2.5 Hz, 1H), 7.03 (dd, *J* = 8.9, 2.6 Hz, 1H), 6.86 (s, 2H), 3.96 (s, 3H), 2.72 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.6, 150.9, 130.4, 128.9, 126.3, 113.8, 113.5, 112.5, 106.0, 97.7, 55.7, 21.7. IR (KBr): 3137, 2925, 2836, 1620, 1535, 1470, 1420, 1359, 1231, 826, 721 cm^{-1}. HRMS (ESI) m/z calculated for $C_{13}H_{13}N_2O$ $[M+H]^+$ 213.1022, found 213.1028.



3d

8-Fluoro-4-methylpyrrolo[1,2-*a*]quinoxaline (3d)

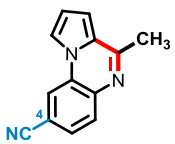
Yellow solid (29.2 mg, 73% yield). PE/EA = 10:1, R_f = 0.25. mp 101-102 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (dd, *J* = 8.9, 5.8 Hz, 1H), 7.84 (s, 1H), 7.54 (dd, *J* = 9.2, 2.6 Hz, 1H), 7.20 (td, *J* = 8.6, 2.6 Hz, 1H), 6.99-6.89 (m, 2H), 2.78 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.0 (d, *J* = 245.6 Hz), 152.8, 132.5, 131.0 (d, *J* = 9.6 Hz), 127.9 (d, *J* = 11.2 Hz), 126.0, 114.4, 114.0, 112.9 (d, *J* = 22.9 Hz), 106.7, 100.4 (d, *J* = 26.7 Hz), 21.8. ^{19}F NMR (376 MHz, $CDCl_3$): δ -111.62. IR (KBr): 3096, 2921, 1619, 1540, 1479, 1421, 1194, 849, 810 cm^{-1}. HRMS (ESI) m/z calculated for $C_{12}H_{10}FN_2$ $[M+H]^+$ 201.0823, found 201.0829.



3e

8-Bromo-4-methylpyrrolo[1,2-*a*]quinoxaline (3e)

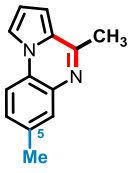
Pale yellow solid (46.3 mg, 89% yield). PE/EA = 10:1, R_f = 0.26. mp 115-116 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, *J* = 1.9 Hz, 1H), 7.90-7.85 (m, 1H), 7.79 (d, *J* = 8.6 Hz, 1H), 7.55 (dd, *J* = 8.6, 2.0 Hz, 1H), 6.98-6.87 (m, 2H), 2.75 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.1, 134.9, 130.7, 128.3, 128.2, 126.2, 120.0, 116.8, 114.4, 114.1, 107.1, 22.0. IR (KBr): 3099, 2919, 1601, 1527, 1476, 1417, 845, 807, 763 cm^{-1}. HRMS (ESI) m/z calculated for $C_{12}H_{10}BrN_2$ $[M+H]^+$ 261.0022, found 261.0030.



3f

4-Methylpyrrolo[1,2-*a*]quinoxaline-8-carbonitrile (3f)

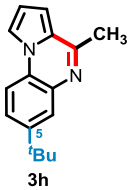
Pale yellow solid (20.7 mg, 50% yield). PE/EA = 5:1, R_f = 0.25. mp 134-135 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (d, *J* = 1.4 Hz, 1H), 8.01-7.89 (m, 2H), 7.67 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.06-6.90 (m, 2H), 2.78 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.9, 138.9, 130.2, 128.0, 127.5, 126.3, 118.5, 118.1, 115.3, 114.7, 109.7, 108.3, 22.1. IR (KBr): 3122, 3016, 2917, 2213, 1608, 1526, 1471, 1417, 1358, 1035, 877, 841, 733 cm^{-1}. HRMS (ESI) m/z calculated for $C_{13}H_{10}N_3$ $[M+H]^+$ 208.0869, found 208.0876.



3g

4,7-Dimethylpyrrolo[1,2-*a*]quinoxaline (3g)

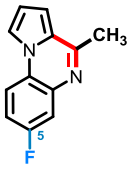
White solid (36.5 mg, 93% yield). PE/EA = 20:1, R_f = 0.25. mp 106-107 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (s, 1H), 7.76 (d, *J* = 7.9 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 1H), 6.96-6.83 (m, 2H), 2.77 (s, 3H), 2.54 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.5, 135.9, 134.8, 129.2, 128.0, 126.2, 125.2, 114.0, 113.3, 113.2, 106.2, 21.9, 21.1. IR (KBr): 3097, 2987, 2915, 2851, 1528, 1491, 1416, 808, 735 cm^{-1}. HRMS (ESI) m/z calculated for $C_{13}H_{13}N_2$ $[M+H]^+$ 197.1073, found 197.1080.



3h

7-(Tert-butyl)-4-methylpyrrolo[1,2-*a*]quinoxaline (3h)

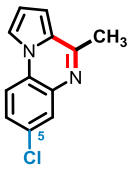
Yellow oil (44.3 mg, 93% yield). PE/EA = 20:1, R_f = 0.29. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, *J* = 2.0 Hz, 1H), 7.91 (s, 1H), 7.79 (d, *J* = 8.6 Hz, 1H), 7.57 (dd, *J* = 8.6, 2.0 Hz, 1H), 6.95-6.83 (m, 2H), 2.77 (s, 3H), 1.46 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.5, 148.4, 135.7, 126.3, 125.8, 125.1, 124.5, 114.0, 113.3, 113.2, 106.2, 34.7, 31.5, 22.0. IR (KBr): 3108, 2959, 2868, 1491, 1455, 1420, 1360, 1269, 811, 712 cm^{-1}. HRMS (ESI) m/z calculated for $C_{16}H_{19}N_2$ $[M+H]^+$ 239.1543, found 239.1548.



3i

7-Fluoro-4-methylpyrrolo[1,2-*a*]quinoxaline (3i)

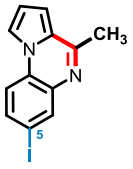
White solid (31.2 mg, 78% yield). PE/EA = 20:1, R_f = 0.30. mp 102-103 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (s, 1H), 7.80 (dd, *J* = 9.0, 5.1 Hz, 1H), 7.62 (dd, *J* = 9.6, 2.7 Hz, 1H), 7.23 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.99-6.82 (m, 2H), 2.76 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.8 (d, *J* = 241.8 Hz), 154.9, 137.1 (d, *J* = 11.5 Hz), 126.1, 124.0, 114.7, 114.6, 114.5, 114.4, 113.6, 106.9, 21.9. ^{19}F NMR (376 MHz, $CDCl_3$): δ -116.78. IR (KBr): 3093, 2919, 1589, 1486, 1422, 1251, 1143, 808, 738 cm^{-1}. HRMS (ESI) m/z calculated for $C_{12}H_{10}FN_2$ $[M+H]^+$ 201.0823, found 201.0829.



3j

7-Chloro-4-methylpyrrolo[1,2-*a*]quinoxaline (3j)

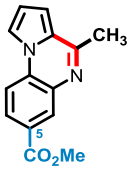
White solid (38.9 mg, 90% yield). PE/EA = 20:1, R_f = 0.29. mp 115-116 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99-7.88 (m, 2H), 7.78 (d, *J* = 8.7 Hz, 1H), 7.48 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.02-6.89 (m, 2H), 2.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.8, 136.9, 130.2, 128.7, 126.8, 126.1, 125.9, 114.7, 114.5, 113.8, 107.1, 21.9. IR (KBr): 3102, 2931, 2847, 1625, 1531, 1492, 1417, 801, 723 cm^{-1}. HRMS (ESI) m/z calculated for $C_{12}H_{10}ClN_2$ $[M+H]^+$ 217.0527, found 217.0534.



3k

7-Iodo-4-methylpyrrolo[1,2-*a*]quinoxaline (3k)

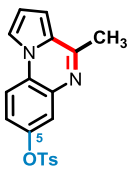
Pale yellow solid (30.8 mg, 50% yield). PE/EA = 20:1, R_f = 0.27. mp 128-129 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (s, 1H), 7.90 (s, 1H), 7.77 (d, *J* = 8.6 Hz, 1H), 7.58 (d, *J* = 8.6 Hz, 1H), 7.01-6.87 (m, 2H), 2.76 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.6, 137.9, 137.2, 135.3, 126.9, 126.1, 115.2, 114.5, 113.9, 107.1, 88.0, 21.9. IR (KBr): 3130, 2993, 2916, 1690, 1476, 1412, 1364, 876, 796, 723 cm^{-1}. HRMS (ESI) m/z calculated for $C_{12}H_{10}IN_2$ $[M+H]^+$ 308.9883, found 308.9892.



3l

Methyl 4-methylpyrrolo[1,2-*a*]quinoxaline-7-carboxylate (3l)

White solid (31.7 mg, 66% yield). PE/EA = 5:1, R_f = 0.33. mp 131-132 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.61 (d, *J* = 1.5 Hz, 1H), 8.18-8.11 (m, 1H), 7.96-7.91 (m, 1H), 7.83 (d, *J* = 8.6 Hz, 1H), 6.96-6.87 (m, 2H), 3.99 (s, 3H), 2.75 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.4, 154.6, 135.5, 131.3, 130.4, 127.8, 126.7, 126.4, 114.8, 114.4, 113.6, 107.3, 52.2, 21.9. IR (KBr): 3103, 2952, 1736, 1614, 1425, 1292, 1202, 1101, 736 cm^{-1}. HRMS (ESI) m/z calculated for $C_{14}H_{13}N_2O_2$ $[M+H]^+$ 241.0972, found 241.0976.

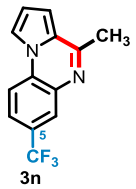


3m

4-Methylpyrrolo[1,2-*a*]quinoxalin-7-yl 4-methylbenzenesulfonate (3m)

Pale yellow solid (52.1 mg, 74% yield). PE/EA = 5:2, R_f = 0.31. mp 133-134 ℃. ^{1}H NMR (400

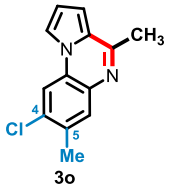
MHz, $CDCl_3$): δ 7.90-7.86 (m, 1H), 7.78 (dd, *J* = 8.6, 4.6 Hz, 3H), 7.48 (d, *J* = 2.5 Hz, 1H), 7.31 (dd, *J* = 17.0, 7.2 Hz, 3H), 6.96-6.87 (m, 2H), 2.72 (s, 3H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.9, 146.4, 145.5, 136.5, 132.3, 129.9, 128.5, 126.1, 126.1, 122.2, 121.4, 114.7, 114.6, 114.0, 107.2, 21.9, 21.7. IR (KBr): 3121, 2922, 2855, 1590, 1485, 1369, 1182, 1091, 834, 739 cm^{-1}. HRMS (ESI) m/z calculated for $C_{19}H_{17}N_2O_3S$ $[M+H]^+$ 353.0954, found 353.0963.



3n

4-Methyl-7-(trifluoromethyl)pyrrolo[1,2-*a*]quinoxaline (3n)

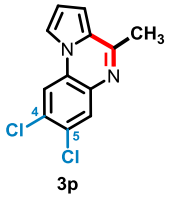
White solid (42.0 mg, 84% yield). PE/EA = 20:1, R_f = 0.33. mp 104-105 ℃. ^1H NMR (400 MHz, $CDCl_3$): δ 8.22 (s, 1H), 8.01-7.88 (m, 2H), 7.78-7.64 (m, 1H), 7.03-6.89 (m, 2H), 2.77 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.1, 135.6, 129.3, 127.2 (q, *J* = 32.9 Hz), 126.8 (q, *J* = 3.9 Hz), 126.3, 124.0 (q, *J* = 270.3 Hz), 123.2 (q, *J* = 3.4 Hz), 114.8, 114.4, 114.2, 107.5, 21.9. ^{19}F NMR (376 MHz, $CDCl_3$): δ -61.97. IR (KBr): 3095, 2911, 2837, 1626, 1535, 1425, 1328, 1170, 1100, 896, 814, 730 cm^{-1}. HRMS (ESI) m/z calculated for $C_{13}H_{10}F_3N_2$ $[M+H]^+$ 251.0791, found 251.0795.



3o

8-Chloro-4,7-dimethylpyrrolo[1,2-*a*]quinoxaline (3o)

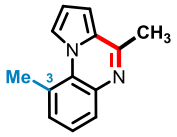
Yellow solid (40.0 mg, 87% yield). PE/EA = 10:1, R_f = 0.27. mp 115-116 ℃. ^1H NMR (400 MHz, $CDCl_3$): δ 7.82 (s, 2H), 7.78 (s, 1H), 6.91 (d, *J* = 3.9 Hz, 1H), 6.90-6.82 (m, 1H), 2.74 (s, 3H), 2.52 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.8, 134.6, 132.9, 132.6, 130.7, 126.1, 126.0, 114.2, 113.9, 113.7, 106.7, 21.9, 19.8. IR (KBr): 3129, 2920, 2853, 1522, 1482, 1414, 1347, 1040, 739, 705 cm^{-1}. HRMS (ESI) m/z calculated for $C_{13}H_{12}ClN_2$ $[M+H]^+$ 231.0684, found 231.0691.



3p

7,8-Dichloro-4-methylpyrrolo[1,2-*a*]quinoxaline (3p)

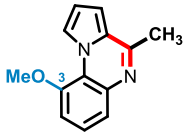
Pale yellow solid (38.0 mg, 76% yield). PE/EA = 10:1, R_f = 0.34. mp 119-120 ℃. ^1H NMR (400 MHz, $CDCl_3$): δ 7.97 (s, 1H), 7.87 (s, 1H), 7.82-7.79 (m, 1H), 6.93 (d, *J* = 3.8 Hz, 1H), 6.92-6.87 (m, 1H), 2.72 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.0, 135.4, 130.3, 130.2, 128.6, 126.7, 126.0, 115.1, 114.7, 114.3, 107.6, 21.9. IR (KBr): 3095, 2921, 2847, 1604, 1520, 1479, 1411, 1127, 882, 739 cm^{-1}. HRMS (ESI) m/z calculated for $C_{12}H_9Cl_2N_2$ $[M+H]^+$ 251.0137, found 251.0144.



3q

4,9-Dimethylpyrrolo[1,2-*a*]quinoxaline (3q)

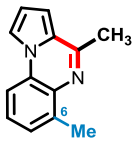
Yellow solid (34.9 mg, 89% yield). PE/EA = 20:1, R_f = 0.32. mp 95-96 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35 (d, *J* = 2.1 Hz, 1H), 7.87 (d, *J* = 7.6 Hz, 1H), 7.40-7.32 (m, 2H), 6.99 (d, *J* = 3.9 Hz, 1H), 6.90 (t, *J* = 3.4 Hz, 1H), 2.99 (s, 3H), 2.79 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.1, 137.1, 130.6, 127.6, 127.5, 125.3, 124.6, 120.2, 113.0, 106.4, 23.8, 21.6. IR (KBr): 3184, 2960, 2917, 1601, 1539, 1418, 1364, 1096, 780, 729 cm^{-1}. HRMS (ESI) m/z calculated for $C_{13}H_{13}N_2$ $[M+H]^+$ 197.1073, found 197.1080.



3r

9-Methoxy-4-methylpyrrolo[1,2-*a*]quinoxaline (3r)

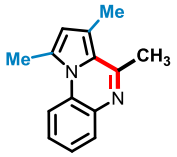
Pale yellow solid (38.6 mg, 91% yield). PE/EA = 10:1, R_f = 0.28. mp 126-127 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.74 (d, *J* = 3.6 Hz, 1H), 7.62-7.54 (m, 1H), 7.36 (t, *J* = 8.1 Hz, 1H), 7.09-7.00 (m, 1H), 6.95 (d, *J* = 4.0 Hz, 1H), 6.88-6.78 (m, 1H), 4.09 (s, 3H), 2.76 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.8, 149.8, 138.1, 126.7, 124.2, 122.0, 121.3, 118.7, 112.4, 108.6, 105.9, 56.1, 21.8. IR (KBr): 3121, 2952, 2837, 1670, 1586, 1540, 1453, 1269, 1100, 788, 735 cm^{-1}. HRMS (ESI) m/z calculated for $C_{13}H_{13}N_2O$ $[M+H]^+$ 213.1022, found 213.1028.



3s

4,6-Dimethylpyrrolo[1,2-*a*]quinoxaline (3s)

Pale yellow solid (33.3 mg, 85% yield). PE/EA = 30:1, R_f = 0.25. mp 110-111 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (s, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 1H), 7.32 (d, *J* = 7.3 Hz, 1H), 6.88 (dt, *J* = 6.5, 3.7 Hz, 2H), 2.81 (d, *J* = 14.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.0, 137.9, 134.7, 127.2, 126.3, 126.2, 126.1, 114.0, 113.3, 111.4, 105.7, 22.2, 18.1. IR (KBr): 3116, 2956, 2915, 1602, 1535, 1474, 1420, 1369, 1064, 733 cm^{-1}. HRMS (ESI) m/z calculated for $C_{13}H_{13}N_2$ $[M+H]^+$ 197.1073, found 197.1079.

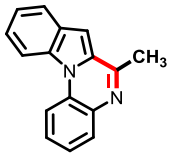


3t

1,3,4-Trimethylpyrrolo[1,2-*a*]quinoxaline (3t)

Pink solid (33.6 mg, 80% yield). PE/EA = 5:1, R_f = 0.38. mp 101-102 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23-8.15 (m, 1H), 7.91-7.83 (m, 1H), 7.43-7.35 (m, 2H), 6.41 (s, 1H), 2.91 (s, 3H), 2.83 (s,

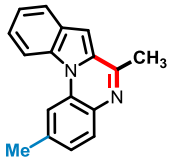
3H), 2.62 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.0, 137.1, 130.0, 128.8, 127.3, 125.5, 124.3, 124.2, 118.2, 117.3, 115.0, 24.4, 17.6, 14.5. IR (KBr): 3063, 2922, 1605, 1530, 1483, 1413, 1345, 851, 810, 743 cm^{-1}. HRMS (ESI) m/z calculated for $C_{14}H_{15}N_2$ $[M+H]^+$ 211.1230, found 211.1237.



3a'

6-Methylindolo[1,2-*a*]quinoxaline (3a')

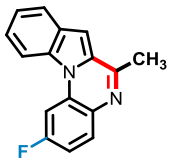
Pale yellow solid (39.9 mg, 86% yield). PE/EA = 10:1, R_f = 0.32. mp 94-95 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.55-8.43 (m, 2H), 8.00 (d, *J* = 8.0 Hz, 2H), 7.60 (dt, *J* = 14.6, 7.9 Hz, 2H), 7.47 (q, *J* = 7.7 Hz, 2H), 7.19 (s, 1H), 2.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.3, 135.9, 133.0, 130.3, 129.8, 129.6, 129.1, 127.8, 124.2, 124.0, 122.7, 122.6, 114.6, 114.5, 100.0, 22.3. IR (KBr): 3051, 2915, 1608, 1532, 1443, 1395, 1361, 785, 733 cm^{-1}. HRMS (ESI) m/z calculated for $C_{16}H_{13}N_2$ $[M+H]^+$ 233.1073, found 233.1080.



3b'

2,6-Dimethylindolo[1,2-*a*]quinoxaline (3b')

Yellow solid (44.8 mg, 91% yield). PE/EA = 10:1, R_f = 0.26. mp 112-113 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.50 (d, *J* = 8.6 Hz, 1H), 8.32 (s, 1H), 8.00 (d, *J* = 7.9 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.59 (t, *J* = 7.7 Hz, 1H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.28 (d, *J* = 8.4 Hz, 1H), 7.19 (s, 1H), 2.85 (s, 3H), 2.66 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.1, 138.1, 133.8, 132.9, 130.1, 129.9, 129.2, 129.1, 125.0, 123.9, 122.6, 122.5, 114.9, 114.6, 99.7, 22.2, 22.1. IR (KBr): 3055, 2919, 2852, 1621, 1539, 1451, 1394, 811, 738 cm^{-1}. HRMS (ESI) m/z calculated for $C_{17}H_{15}N_2$ $[M+H]^+$ 247.1230, found 247.1235.

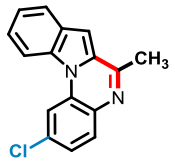


3c'

2-Fluoro-6-methylindolo[1,2-*a*]quinoxaline (3c')

Yellow solid (42.0 mg, 84% yield). PE/EA = 10:1, R_f = 0.25. mp 124-125 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (d, *J* = 8.6 Hz, 1H), 8.08 (dd, *J* = 10.4, 2.5 Hz, 1H), 7.99-7.89 (m, 2H), 7.56 (t, *J* = 7.7 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.18-7.10 (m, 2H), 2.79 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.5 (d, *J* = 245.3 Hz), 154.3, 132.8, 132.4, 130.9 (d, *J* = 9.8 Hz), 130.7 (d, *J* = 11.6 Hz), 129.3, 129.2, 124.5, 122.9, 122.7, 114.1, 111.2 (d, *J* = 22.6 Hz), 101.9 (d, *J* = 28.3 Hz), 100.4, 22.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ: -110.54. IR (KBr): 3056, 2918, 2847, 1621, 1551, 1489, 1456, 1398, 1206, 1160, 820, 735 cm^{-1}. HRMS (ESI) m/z calculated for $C_{16}H_{12}FN_2$ $[M+H]^+$ 251.0979, found

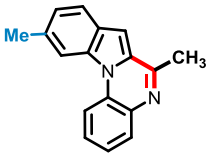
251.0984.



3d'

2-Chloro-6-methylindolo[1,2-*a*]quinoxaline (3d')

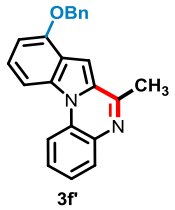
Yellow solid (38.8 mg, 73% yield). PE/EA = 10:1, R_f = 0.28. mp 130-131 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.42 (s, 1H), 8.40-8.32 (m, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 8.5 Hz, 1H), 7.60 (t, *J* = 7.7 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.40 (d, *J* = 8.5 Hz, 1H), 7.19 (s, 1H), 2.82 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.4, 134.4, 133.1, 132.8, 130.7, 130.4, 129.4, 129.1, 124.6, 124.2, 123.0, 122.8, 114.6, 114.3, 100.6, 22.2. IR (KBr): 3059, 2921, 2852, 1609, 1538, 1449, 1396, 819, 738 cm^{-1}. HRMS (ESI) m/z calculated for $C_{16}H_{12}ClN_2$ $[M+H]^+$ 267.0684, found 267.0690.



3e'

6,10-Dimethylindolo[1,2-*a*]quinoxaline (3e')

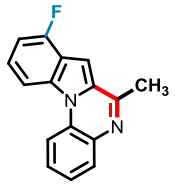
Yellow solid (42.3 mg, 86% yield). PE/EA = 10:1, R_f = 0.29. mp 102-103 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.49 (d, *J* = 8.3 Hz, 1H), 8.26 (s, 1H), 7.98 (d, *J* = 7.9 Hz, 1H), 7.87 (d, *J* = 8.2 Hz, 1H), 7.65-7.57 (m, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.31 (d, *J* = 10.7 Hz, 1H), 7.15 (s, 1H), 2.83 (s, 3H), 2.70 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.3, 135.8, 134.5, 133.5, 130.4, 129.5, 129.4, 127.6, 127.0, 124.6, 123.9, 122.2, 114.6, 114.3, 100.1, 22.6, 22.2. IR (KBr): 3026, 2914, 2854, 1605, 1533, 1435, 1397, 809, 733 cm^{-1}. HRMS (ESI) m/z calculated for $C_{17}H_{15}N_2$ $[M+H]^+$ 247.1230, found 247.1236.



3f'

8-(Benzyloxy)-6-methylindolo[1,2-*a*]quinoxaline (3f')

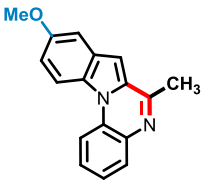
Pale yellow solid (60.2 mg, 89% yield). PE/EA = 5:1, R_f = 0.30. mp 165-166 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.41 (d, *J* = 8.3 Hz, 1H), 8.04-7.93 (m, 2H), 7.64-7.53 (m, 3H), 7.54-7.38 (m, 5H), 7.34 (s, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 5.33 (s, 2H), 2.82 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.4, 153.5, 137.0, 136.1, 134.1, 130.2, 129.4, 128.8, 128.6, 128.1, 127.5, 125.1, 124.1, 120.9, 114.7, 107.7, 102.8, 97.7, 70.1, 22.3. IR (KBr): 3036, 2926, 2869, 1671, 1436, 1393, 1258, 743, 700 cm^{-1}. HRMS (ESI) m/z calculated for $C_{23}H_{19}N_2O$ $[M+H]^+$ 339.1492, found 339.1501.



3g'

8-Fluoro-6-methylindolo[1,2-*a*]quinoxaline (3g')

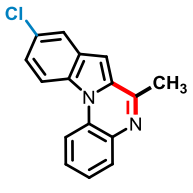
Yellow solid (31.5 mg, 63% yield). PE/EA = 20:1, R_f = 0.25. mp 136-137 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.45-8.36 (m, 1H), 8.17 (d, *J* = 8.6 Hz, 1H), 8.03-7.93 (m, 1H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.46 (q, *J* = 7.7 Hz, 2H), 7.23 (s, 1H), 7.18-7.05 (m, 1H), 2.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.1 (d, *J* = 248.6 Hz), 155.2, 135.9, 134.9 (d, *J* = 9.7 Hz), 129.8, 129.6, 127.9, 124.6 (d, *J* = 7.5 Hz), 124.5, 118.9 (d, *J* = 23.0 Hz), 114.6, 110.6 (d, *J* = 3.9 Hz), 106.9 (d, *J* = 18.1 Hz), 95.7, 22.2. ^{19}F NMR (376 MHz, $CDCl_3$): δ -119.41. IR (KBr): 3026, 2919, 2863, 1603, 1573, 1498, 1467, 1233, 741 cm^{-1}. HRMS (ESI) m/z calculated for $C_{16}H_{12}FN_2$ $[M+H]^+$ 251.0979, found 251.0984.



3h'

9-Methoxy-6-methylindolo[1,2-*a*]quinoxaline (3h')

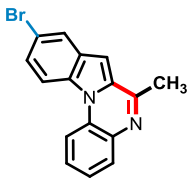
Pale yellow solid (47.2 mg, 90% yield). PE/EA = 5:1, R_f = 0.27. mp 127-128 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36 (d, *J* = 8.3 Hz, 1H), 8.29 (d, *J* = 9.3 Hz, 1H), 7.98 (d, *J* = 7.9 Hz, 1H), 7.57 (t, *J* = 7.8 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.30 (d, *J* = 2.4 Hz, 1H), 7.19 (dd, *J* = 9.3, 2.5 Hz, 1H), 7.05 (s, 1H), 3.97 (s, 3H), 2.81 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.7, 154.6, 135.6, 130.2, 130.1, 130.0, 129.5, 128.3, 127.7, 123.8, 115.4, 114.2, 102.4, 99.5, 55.6, 22.2. IR (KBr): 3002, 2922, 2835, 1616, 1456, 1398, 1211, 1026, 841, 742 cm^{-1}. HRMS (ESI) m/z calculated for $C_{17}H_{15}N_2O$ $[M+H]^+$ 263.1179, found 263.1183.



3i'

9-Chloro-6-methylindolo[1,2-*a*]quinoxaline (3i')

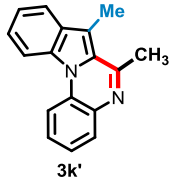
Yellow solid (39.9 mg, 75% yield). PE/EA = 10:1, R_f = 0.25. mp 136-137 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.42 (dd, *J* = 12.3, 8.8 Hz, 2H), 8.06 (d, *J* = 7.9 Hz, 1H), 7.96 (s, 1H), 7.65 (t, *J* = 7.7 Hz, 1H), 7.57-7.46 (m, 2H), 7.16 (s, 1H), 2.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.0, 135.7, 131.3, 130.7, 130.1, 129.8, 129.8, 128.4, 128.3, 124.5, 124.4, 121.7, 115.6, 114.4, 99.4, 22.2. IR (KBr): 3057, 2921, 2849, 1613, 1536, 1442, 1396, 876, 746 cm^{-1}. HRMS (ESI) m/z calculated for $C_{16}H_{12}ClN_2$ $[M+H]^+$ 267.0684, found 267.0690.



3j'

9-Bromo-6-methylindolo[1,2-*a*]quinoxaline (3j')

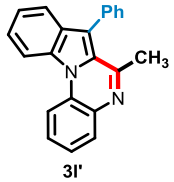
Yellow solid (37.2 mg, 60% yield). PE/EA = 10:1, R_f = 0.27. mp 152-153 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (d, *J* = 8.3 Hz, 1H), 8.29 (s, 1H), 8.15 (d, *J* = 9.0 Hz, 1H), 7.99 (d, *J* = 7.9 Hz, 1H), 7.75 (d, *J* = 9.0 Hz, 1H), 7.60 (t, *J* = 7.7 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.02 (s, 1H), 2.81 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.0, 135.8, 132.3, 131.9, 131.4, 131.2, 130.1, 129.8, 128.0, 124.4, 116.1, 114.5, 98.8, 86.7, 22.3. IR (KBr): 3058, 2920, 2851, 1613, 1537, 1440, 1393, 869, 748 cm^{-1}. HRMS (ESI) m/z calculated for $C_{16}H_{12}BrN_2$ $[M+H]^+$ 311.0178, found 311.0186.



3k'

6,7-Dimethylindolo[1,2-*a*]quinoxaline (3k')

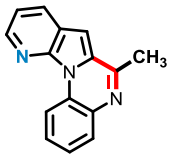
Yellow solid (34.5 mg, 70% yield). PE/EA = 10:1, R_f = 0.27. mp 111-112 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.43-8.35 (m, 2H), 7.92 (dd, *J* = 13.7, 7.5 Hz, 2H), 7.54 (q, *J* = 9.8, 9.2 Hz, 2H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 2.95 (s, 3H), 2.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.9, 135.4, 131.8, 130.5, 129.9, 129.1, 127.6, 126.7, 124.5, 123.6, 121.9, 120.5, 114.4, 114.3, 109.7, 25.6, 11.2. IR (KBr): 3058, 2921, 2854, 1607, 1536, 1481, 1449, 1394, 1372, 858, 731 cm^{-1}. HRMS (ESI) m/z calculated for $C_{17}H_{15}N_2$ $[M+H]^+$ 247.1230, found 247.1233.



3l'

6-Methyl-7-phenylindolo[1,2-*a*]quinoxaline (3l')

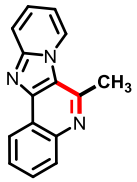
Yellow solid (40.7 mg, 66% yield). PE/EA = 20:1, R_f = 0.26. mp 99-100 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.58-8.46 (m, 2H), 7.98 (d, *J* = 7.9 Hz, 1H), 7.70 (d, *J* = 8.1 Hz, 1H), 7.66-7.50 (m, 7H), 7.44 (q, *J* = 7.4 Hz, 2H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.8, 135.7, 134.8, 131.7, 131.5, 130.3, 130.2, 129.3, 128.1, 127.7, 125.9, 124.7, 124.0, 122.6, 121.7, 116.4, 114.6, 114.3, 25.3. IR (KBr): 3058, 2923, 2850, 1602, 1541, 1446, 1393, 1371, 1256, 743, 701 cm^{-1}. HRMS (ESI) m/z calculated for $C_{22}H_{17}N_2$ $[M+H]^+$ 309.1386, found 309.1394.



3m'

6-Methylpyrido[3',2':4,5]pyrrolo[1,2-*a*]quinoxaline (3m')

Yellow solid (19.6 mg, 42% yield). PE/EA = 10:1, R_f = 0.27. mp 123-124 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.89 (dd, *J* = 8.4, 1.4 Hz, 1H), 8.75 (dd, *J* = 4.5, 1.5 Hz, 1H), 8.29 (dd, *J* = 8.1, 1.6 Hz, 1H), 8.01 (d, *J* = 7.9 Hz, 1H), 7.74-7.63 (m, 1H), 7.53-7.47 (m, 1H), 7.44 (dd, *J* = 8.1, 4.5 Hz, 1H), 7.11 (s, 1H), 2.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.7, 144.8, 135.2, 130.3, 129.0, 128.9, 128.7, 128.4, 124.6, 121.0, 118.5, 117.5, 96.7, 22.0. IR (KBr): 3058, 2923, 2850, 1673, 1602, 1541, 1446, 1394, 743, 701 cm^{-1}. HRMS (ESI) m/z calculated for $C_{15}H_{12}N_3$ $[M+H]^+$ 234.1026, found 234.1032.

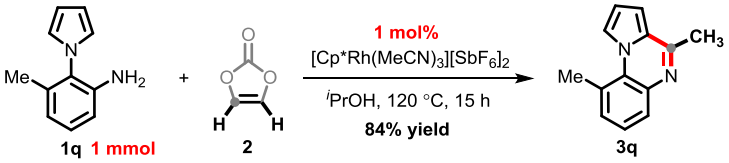


3n'

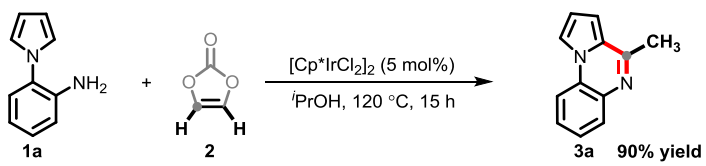
6-Methylpyrido[2',1':2,3]imidazo[4,5-*c*]quinoline (3n')

Pale Yellow solid (7.0 mg, 15% yield). PE/EA = 1:2, R_f = 0.25. mp 137-138 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.90 (d, *J* = 7.0 Hz, 1H), 8.75 (d, *J* = 8.0 Hz, 1H), 8.22 (d, *J* = 8.3 Hz, 1H), 7.97 (d, *J* = 9.2 Hz, 1H), 7.84-7.77 (m, 1H), 7.71 (t, *J* = 7.5 Hz, 1H), 7.65-7.58 (m, 1H), 7.11 (t, *J* = 7.4 Hz, 1H), 3.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.3, 146.7, 145.8, 144.8, 129.4, 128.7, 128.6, 127.2, 126.1, 122.6, 121.7, 121.4, 118.3, 112.6, 24.2. IR (KBr): 3056, 2922, 2854, 1632, 1569, 1499, 1428, 1361, 1264, 750 cm^{-1}. HRMS (ESI) m/z calculated for $C_{15}H_{12}N_3$ $[M+H]^+$ 234.1026, found 234.1032.

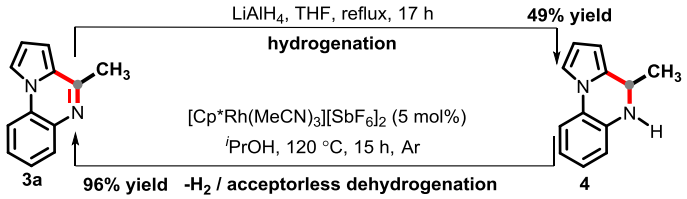
D. Large-scale transformation and further derivatization:



A pressure tube was charged with $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (1 mol%), 3-methyl-2-(1*H*-pyrrol-1-yl)aniline **1q** (1.2 mmol), vinylene carbonate **2** (1.0 mmol), ^{i}PrOH (3.0 mL). The reaction mixture was stirred at 120 ℃ for 15 h under Ar condition. After cooling to room temperature, the mixture was filtered through a short Celite pad and all volatiles were removed under reduced pressure. The residue was purified by silica gel chromatography to afford the product **3q** (164.7 mg, 84% yield).



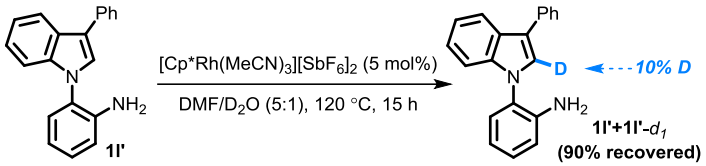
A pressure tube was charged with $[Cp^*IrCl_2]_2$ (5 mol%), 2-(1*H*-pyrrol-1-yl)aniline **1a** (0.12 mmol), vinylene carbonate **2** (0.1 mmol), ^{i}PrOH (0.5 mL). The reaction mixture was stirred at 120 ℃ for 15 h under Ar condition. After cooling to room temperature, the mixture was filtered through a short Celite pad and all volatiles were removed under reduced pressure. The residue was purified by silica gel chromatography to afford the product **3a** (16.4 mg, 90% yield).



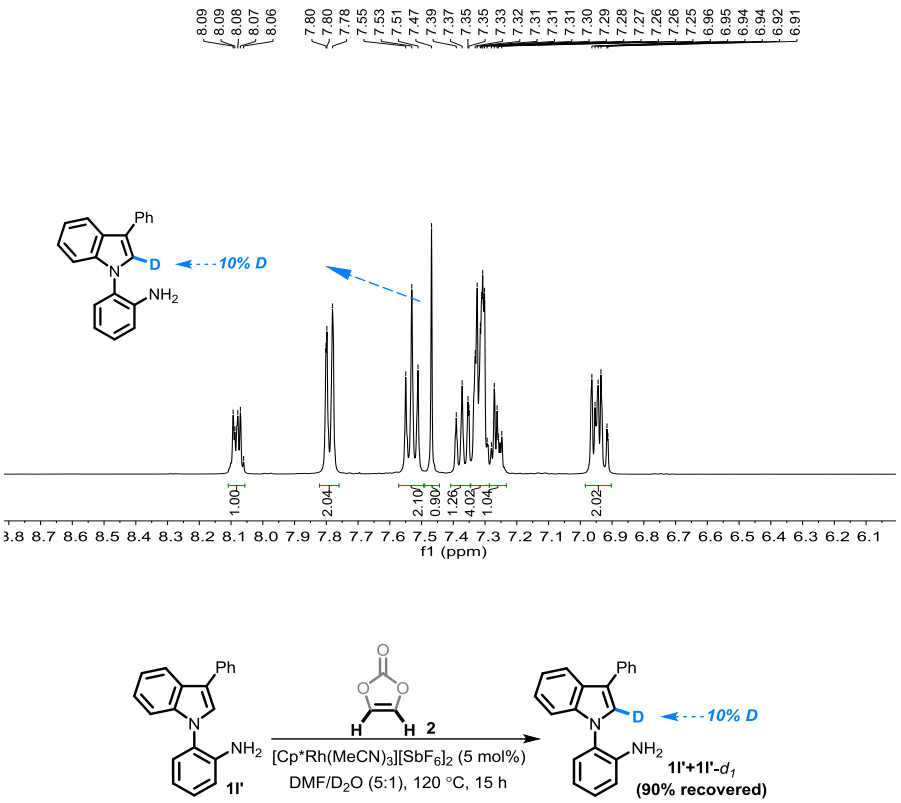
To a stirred solution of 4-methylpyrrolo[1,2-*a*]quinoxaline **3a** (0.2 mmol) in anhydrous THF (2 mL), $LiAlH_4$ (0.8 mmol) was added portion wise. The reaction was refluxed with stirring for 17 h under Ar condition. After cooling to room temperature, the reaction was quenched with ethyl acetate and all volatiles were removed under reduced pressure. The residue was purified by silica gel chromatography to afford the product **4** (18.0 mg, 49% yield). PE/EA = 20:1, R_f = 0.33. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (d, *J* = 7.9 Hz, 1H), 7.20 (s, 1H), 7.01 (t, *J* = 7.6 Hz, 1H), 6.87 (t, *J* = 7.7 Hz, 1H), 6.79 (d, *J* = 7.8 Hz, 1H), 6.36 (t, *J* = 3.1 Hz, 1H), 6.09-6.02 (m, 1H), 4.61 (q, *J* = 6.3 Hz, 1H), 3.91 (s, 1H), 1.61 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.4, 131.2, 124.6, 119.2, 115.3, 114.7, 114.3, 110.1, 103.3, 46.5, 20.6.

A pressure tube was charged with $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (5 mol%), 4-methyl-4,5-dihydropyrrolo[1,2-*a*]quinoxaline **4** (0.1 mmol), ^{i}PrOH (0.5 mL). The reaction mixture was stirred at 120 ℃ for 15 h under Ar condition. After cooling to room temperature, the mixture was filtered through a short Celite pad and all volatiles were removed under reduced pressure. The residue was purified by silica gel chromatography to afford the product **3a** (17.5 mg, 96% yield).

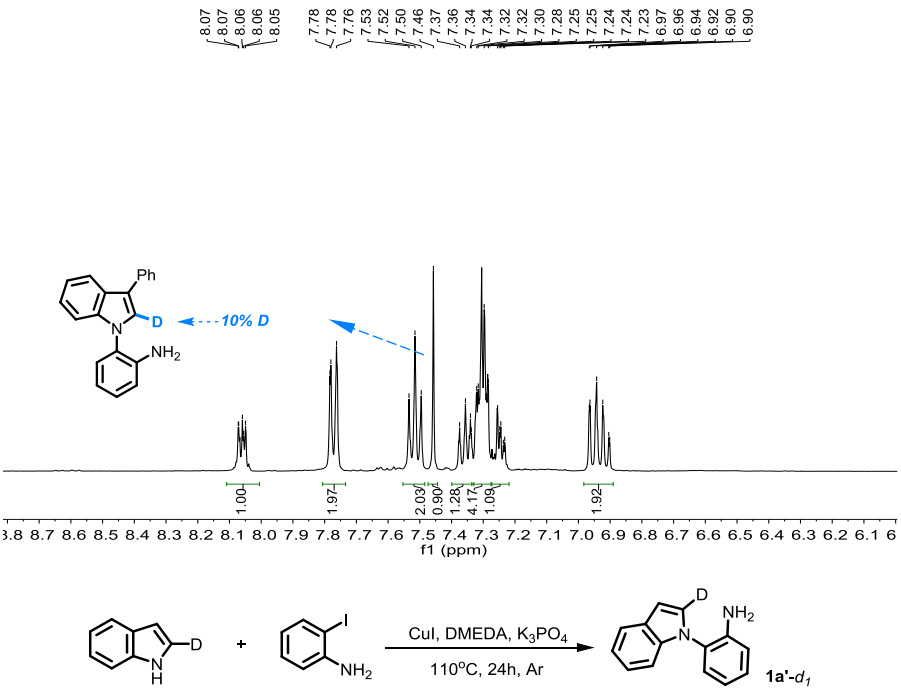
E. Mechanistic studies:



A pressure tube was charged with $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (5 mol%), 2-(3-phenyl-1*H*-indol-1-yl)aniline **1l'** (0.1 mmol), D_2O (0.1 mL) and DMF (0.5 mL). The reaction mixture was stirred at 120 ℃ for 15 h under Ar condition. After cooling to room temperature, the mixture was filtered through a short Celite pad and all volatiles were removed under reduced pressure. The residue was purified by silica gel chromatography to afford **1l'** and **1l'**-d_1 in 90% yield with 10% deuteration.

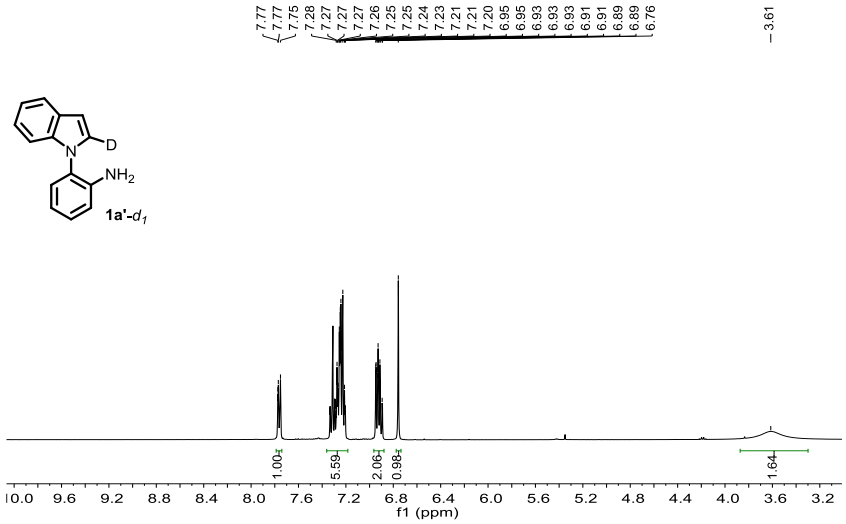


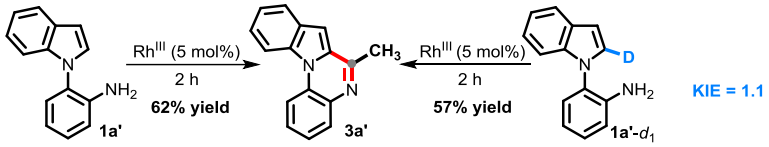
A pressure tube was charged with $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (5 mol%), 2-(3-phenyl-1*H*-indol-1-yl)aniline **1l'** (0.1 mmol), vinylene carbonate **2** (0.1 mmol), D_2O (0.1 mL) and DMF (0.5 mL). The reaction mixture was stirred at 120 ℃ for 15 h under Ar condition. After cooling to room temperature, the mixture was filtered through a short Celite pad and all volatiles were removed under reduced pressure. The residue was purified by silica gel chromatography to afford **1l'** and **1l'**-d_1 in 90% yield with 10% deuteration.



Compounds **1a'**-d_1 were prepared in the following method. A pressure tube was charged with

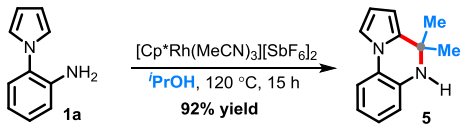
1*H*-indole-2-*d* (1.0 mmol), 2-iodoanilines (1.5 mmol), CuI (20 mol%), DMEDA (*N*,*N*'-Dimethyl-1,2-ethanediamine, 80 mol%), K_3PO_4 (2.1 mmol), and toluene (2.0 mL). The mixture was stirred at 110 ℃ for 24 h under argon. After cooling to room temperature, the mixture was filtered and additional ethyl acetate was used to elute the silica gel. The filtrate was concentrated and the resulting residue was purified by column chromatography to afford the product **1a**'-d_1. Pale yellow oil (163.1 mg, 78% yield). PE/EA = 10:1, R_f = 0.32. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79-7.74 (m, 1H), 7.34-7.29 (m, 1H), 7.29-7.20 (m, 4H), 6.96-6.88 (m, 2H), 6.76 (s, 1H), 3.61 (s, 2H).





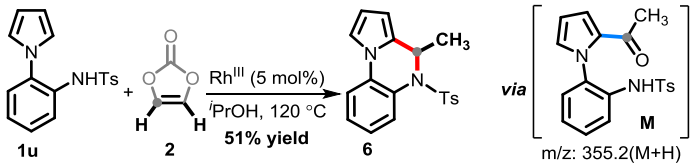
A pressure tube was charged with $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (5 mol%), 2-(1*H*-indol-1-yl)aniline **1a**' (0.12 mmol), vinylene carbonate **2** (0.1 mmol), and ^{i}PrOH (0.5 mL). The reaction mixture was stirred at 120 ℃ for 2 h under Ar condition. After cooling to room temperature, the mixture was filtered and all volatiles were removed under reduced pressure. The residue was purified by silica gel chromatography to afford the product **3a**' (14.4 mg, 62% yield).

A pressure tube was charged with $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (5 mol%), 2-(1*H*-indol-1-yl-2-*d*)aniline **1a**'-d_1 (0.12 mmol), vinylene carbonate **2** (0.1 mmol), and ^{i}PrOH (0.5 mL). The reaction mixture was stirred at 120 ℃ for 2 h under Ar condition. After cooling to room temperature, the mixture was filtered and all volatiles were removed under reduced pressure. The residue was purified by silica gel chromatography to afford the product **3a**' (13.2 mg, 57% yield).



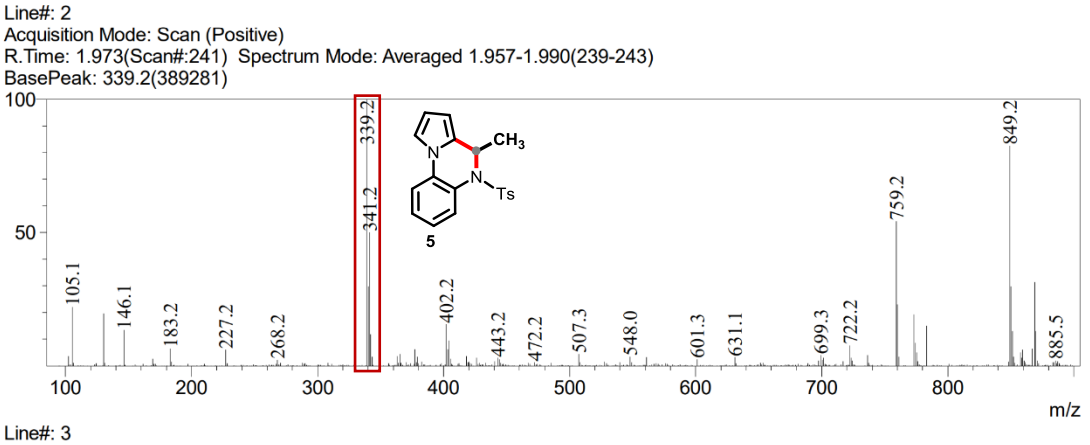
A pressure tube was charged with $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (5 mol%), 2-(1*H*-pyrrol-1-yl)aniline **1a** (0.1 mmol), and ^{i}PrOH (0.5 mL). The reaction mixture was stirred at 120 ℃ for 15 h under Ar condition. After cooling to room temperature, the mixture was filtered and all volatiles were removed under reduced pressure. The residue was purified by silica gel chromatography to

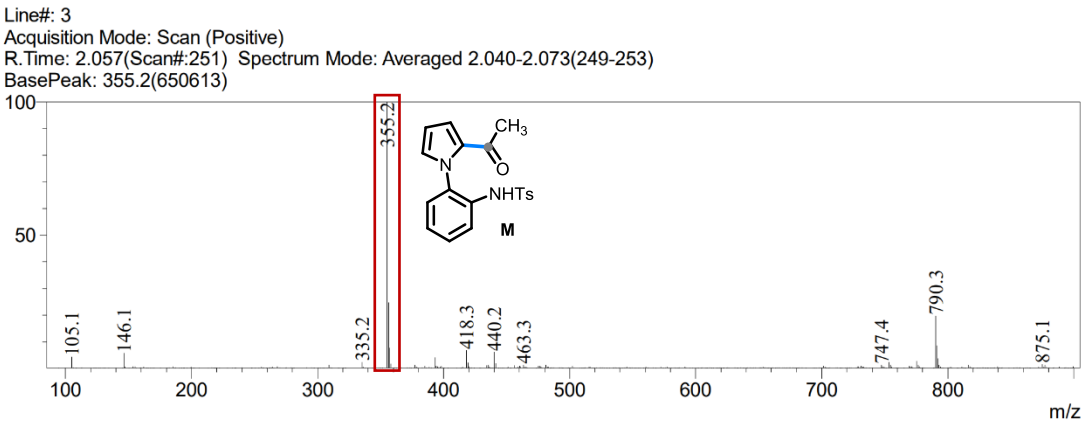
afford the product **5**[15] (18.2 mg, 92% yield). PE/EA = 20:1, R_f = 0.34. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (d, *J* = 7.9 Hz, 1H), 7.17 (s, 1H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.86 (t, *J* = 7.6 Hz, 1H), 6.77 (d, *J* = 7.8 Hz, 1H), 6.33 (t, *J* = 2.9 Hz, 1H), 6.07-6.01 (m, 1H), 3.71 (s, 1H), 1.56 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.3, 134.7, 125.3, 124.6, 119.0, 115.7, 114.6, 113.9, 109.9, 101.8, 51.4, 29.5.

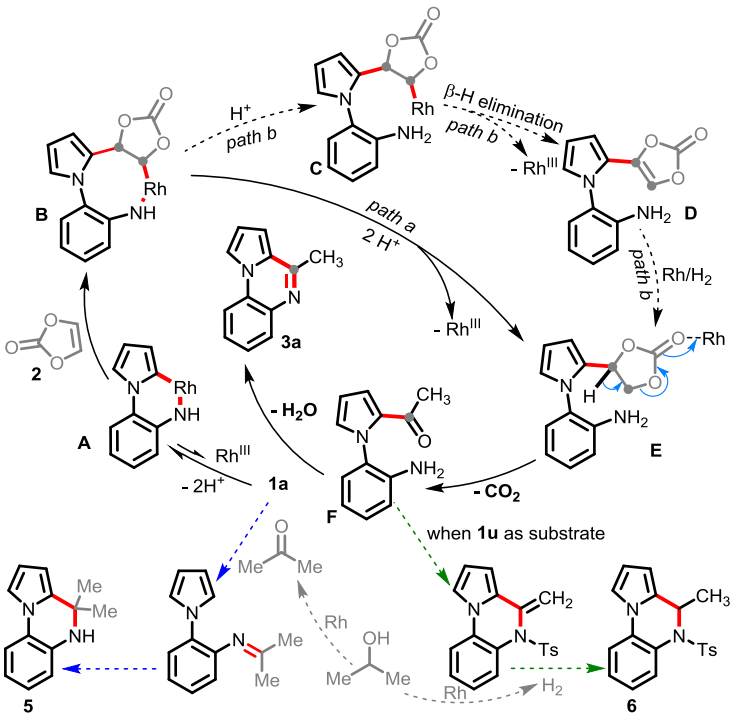


A pressure tube was charged with [Cp*Rh(MeCN)$_3$][SbF$_6$]$_2$ (5 mol%), *N*-(2-(1*H*-pyrrol-1-yl)phenyl)-4-methylbenzenesulfonamide **1u** (0.12 mmol), vinylene carbonate **2** (0.1 mmol), and ^{i}PrOH (0.5 mL). The reaction mixture was stirred at 120 ℃ for 15 h under Ar condition. After cooling to room temperature, the mixture was filtered through a short Celite pad and all volatiles were removed under reduced pressure. The residue was purified by silica gel chromatography to afford the product **6** (17.2 mg, 51% yield). PE/EA = 10:1, R_f = 0.32. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 8.0 Hz, 1H), 7.33 (t, *J* = 7.7 Hz, 1H), 7.24 (t, *J* = 7.7 Hz, 1H), 7.18 (d, *J* = 7.9 Hz, 1H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.88 (d, *J* = 7.9 Hz, 2H), 6.64-6.57 (m, 1H), 6.05 (d, *J* = 3.0 Hz, 1H), 5.91-5.82 (m, 1H), 5.60 (q, *J* = 7.0 Hz, 1H), 2.26 (s, 3H), 1.33 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.0, 133.9, 131.8, 130.1, 129.2, 128.6, 128.0, 126.8, 125.0, 124.4, 115.1, 113.9, 110.2, 104.9, 50.3, 22.3, 21.3. IR (KBr): 2972, 2923, 2854, 1595, 1502, 1347, 1165, 1076, 752, 706, 575 cm^{-1}. HRMS (ESI) m/z calculated for $C_{19}H_{19}N_2O_2S$ $[M+H]^+$ 339.1162, found 339.1168.

The part of the crude product was taken for mass spectrometry, the spectra as followed:







Possible reaction pathways

F. Antimicrobial assay:

Staphylococcus aureus, drug-resistant *Staphylococcus aureus* 171, *Escherichia coli*, *Salmonella*, *Pseudomonas aeruginosa* and drug-resistant *Pseudomonas aeruginosa* 756 used in this paper are all from Huashan Hospital affiliated to Fudan University (Shanghai, China).

Gram-positive bacteria (*S. aureus*, drug-resistant *S. aureus* 171) and Gram-negative bacteria (*E. coli*, *Salmonella*, *P. aeruginosa* and drug-resistant *P. aeruginosa* 756) were used as testing bacteria. Vancomycin, ceftazidime and levofloxacin were used as positive control. The results of antibacterial activities were discussed based on minimum inhibitory concentration (MIC). Tested compounds were set at 128, 64, 32, 16, 8, 4, 2, 1 and 0 μg/mL in DMSO, respectively. The tested strains were incubated in liquid mediums, the medium was made up of beef extract (3.0 g/L), peptone (10.0 g/L), NaCl (5.0 g/L) and pH 7.0, and the temperature of culture was 37 ℃. Different fresh strains taken from the culture mediums were immediately diluted into 2.0 mL sterilized water, and the final concentrations of the spores of different fungi were approximately 1×10^6 CFU/mL in water. Each well containing 100 μL of the solution of the sample was inoculated with 100 μL of bacteria suspension containing 10^6 CFU/mL and then incubated at 37 ℃ for 24 h. The activities were compared with the same concentrations (128 μg/mL in H_2O) of the known vancomycin against *S. aureus*, ceftazidime against *E. coli* and *P. aeruginosa*, levofloxacin against *Salmonella*. The results of Antibacterial activity (MIC) were shown in Table 1.

Table 1. Antibacterial activity (MIC)

Compounds	MIC ($mg \cdot mL^{-1}$)					
	Gram-positive bacteria		Gram-negative bacteria			
	S. aureus	Drug-resistant *S. aureus* 171	*E. coli*	*Salmonella*	*P. aeruginosa*	Drug-resistance *P. aeruginosa* 756
3a	＞128	**32**	＞128	＞128	**64**	＞128
3b	**64**	**32**	＞128	＞128	＞128	＞128
3c	＞128	**64**	**64**	＞128	＞128	＞128
3f	＞128	**64**	＞128	＞128	＞128	＞128
3i	＞128	**64**	＞128	＞128	＞128	＞128
3m	＞128	＞128	＞128	**64**	**64**	**128**
3n	＞128	**64**	＞128	**64**	＞128	**64**
3s	**64**	＞128	＞128	＞128	＞128	＞128
3m'	＞128	**64**	**64**	＞128	＞128	＞128
Moxifloxacin	128	128	128	128	128	128

G. References:

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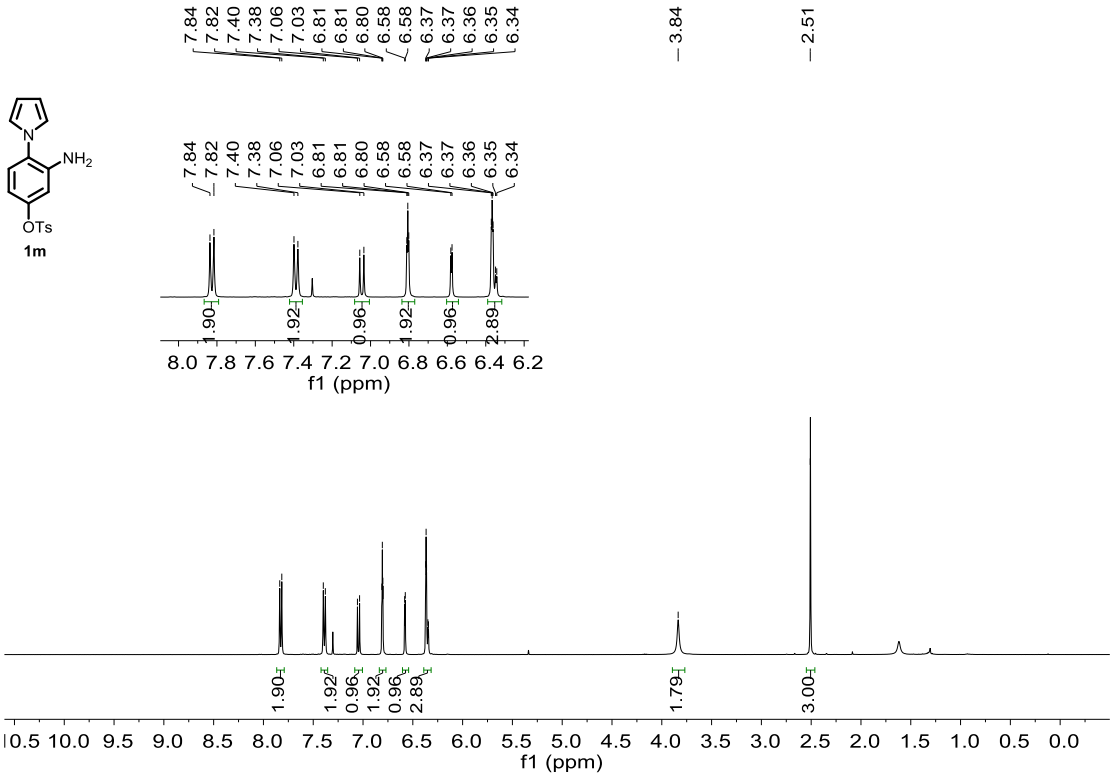
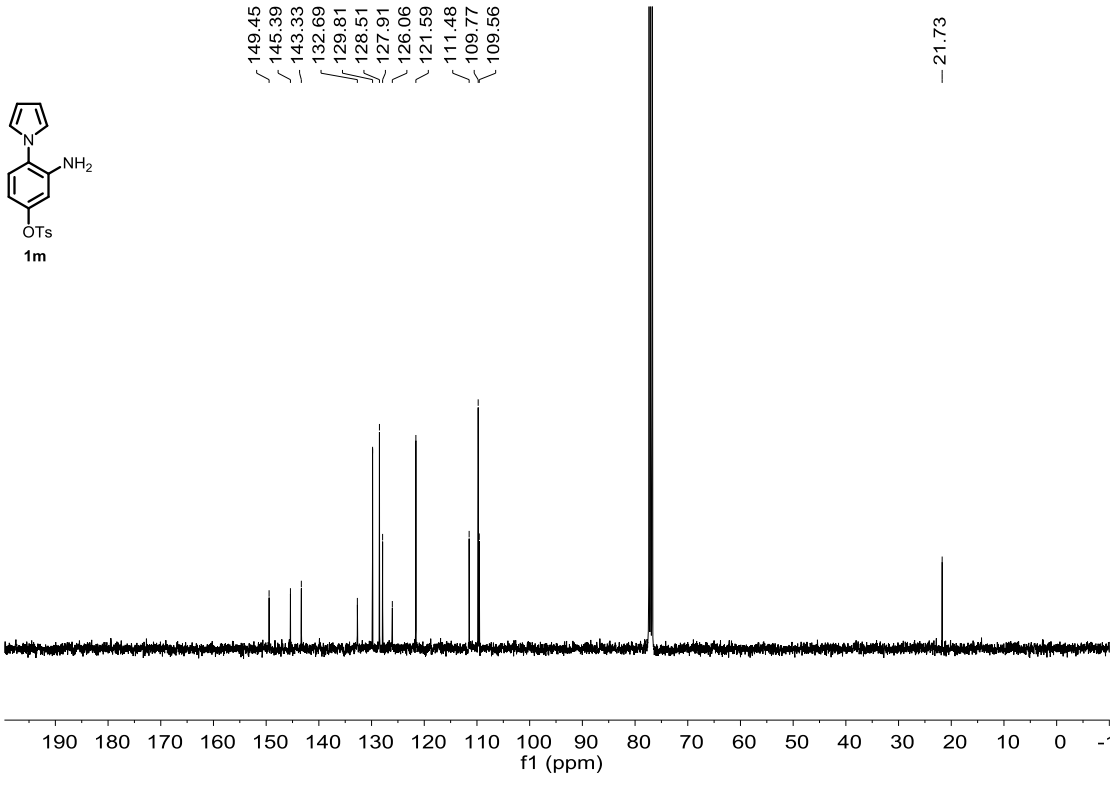
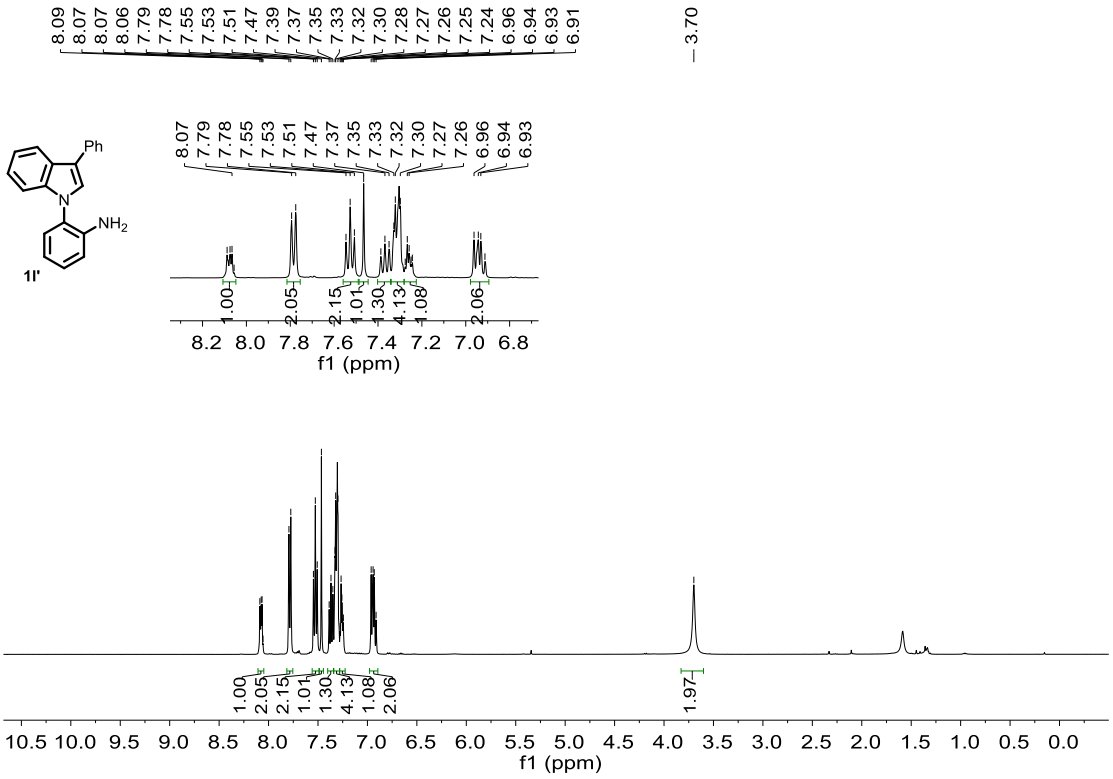
H. NMR spectra:



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7.30
7.28
7.27
7.26
7.25
7.24
6.96
6.94
6.93
6.91
3.70
Ph
N
NH2
1l'
8.07
7.79
7.78
7.55
7.53
7.51
7.47
7.37
7.35
7.33
7.32
7.30
7.27
7.26
6.96
6.94
6.93
1.00
2.05
2.15
1.01
1.30
4.13
1.08
2.06
8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8
f1 (ppm)
1.00
2.05
2.15
1.01
1.30
4.13
1.08
2.06
1.97
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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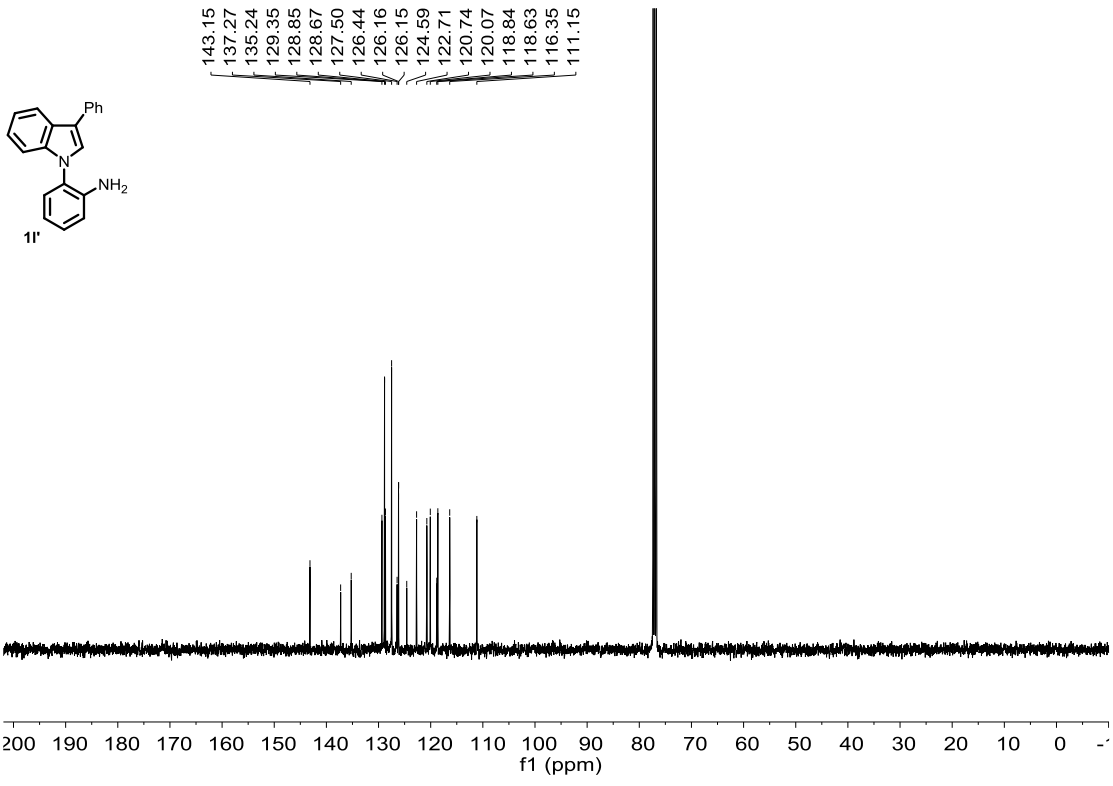
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120.07
118.84
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Ph
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NH2
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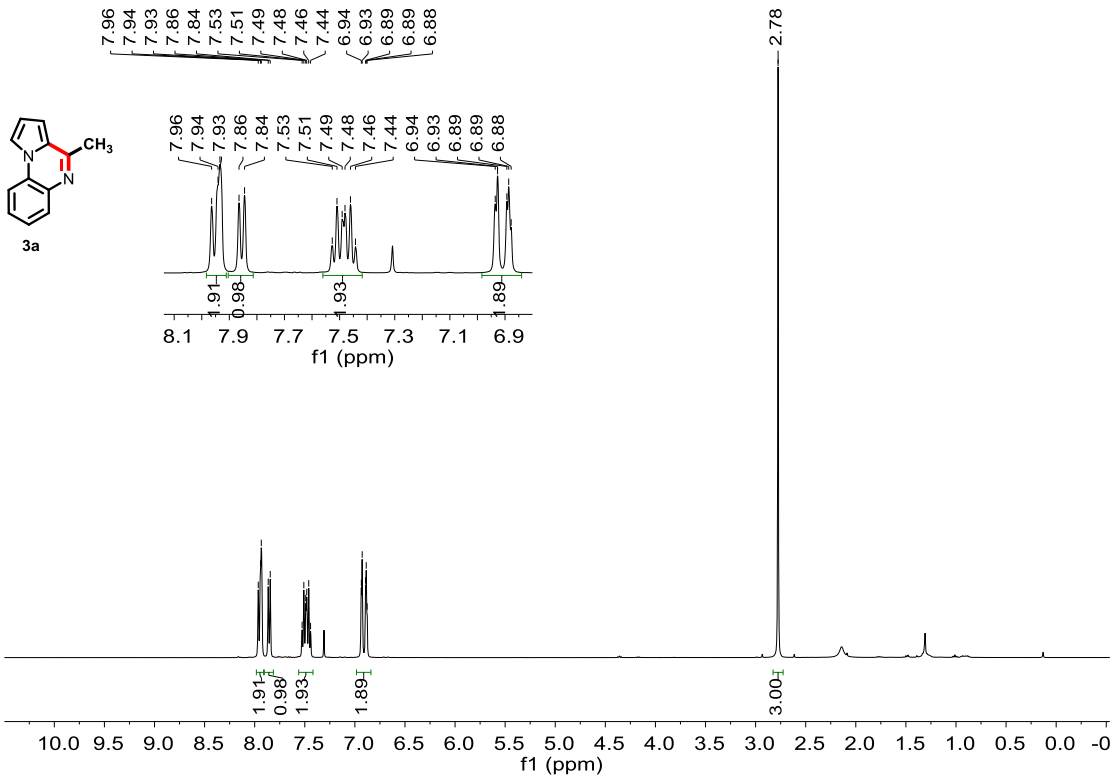
f1 (ppm)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6.89
6.89
6.88
2.78
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N
3a
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0.98
1.93
1.89
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0.98
1.93
1.89
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
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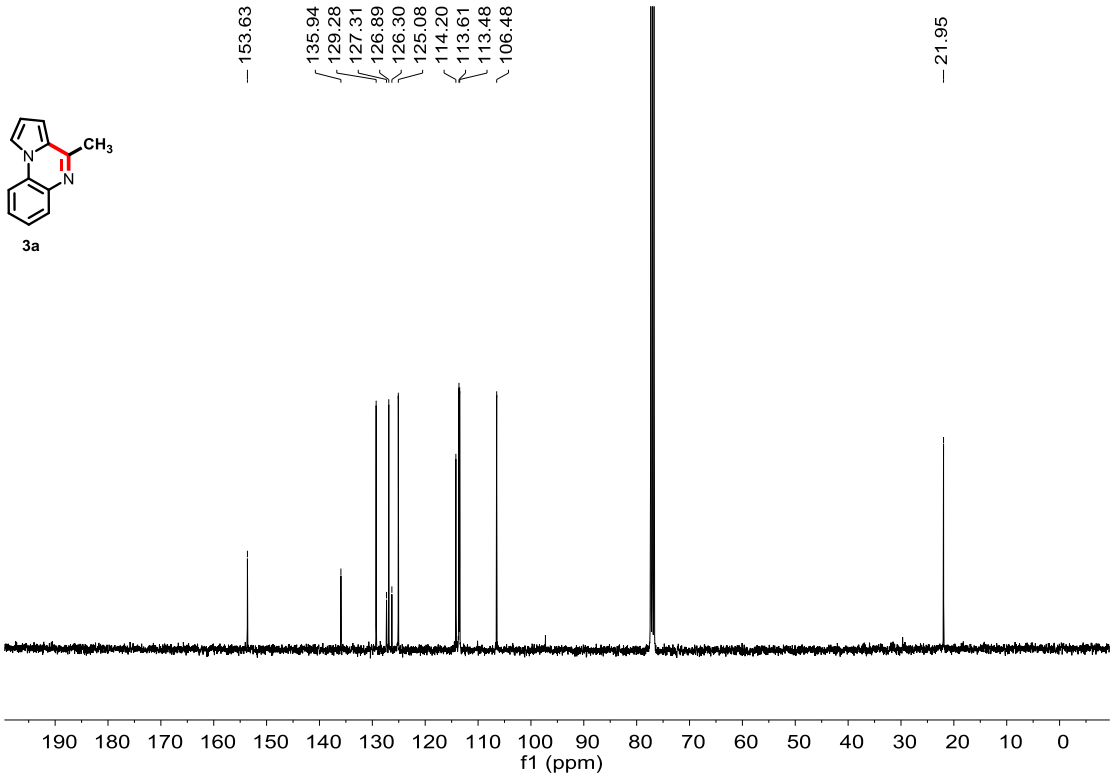
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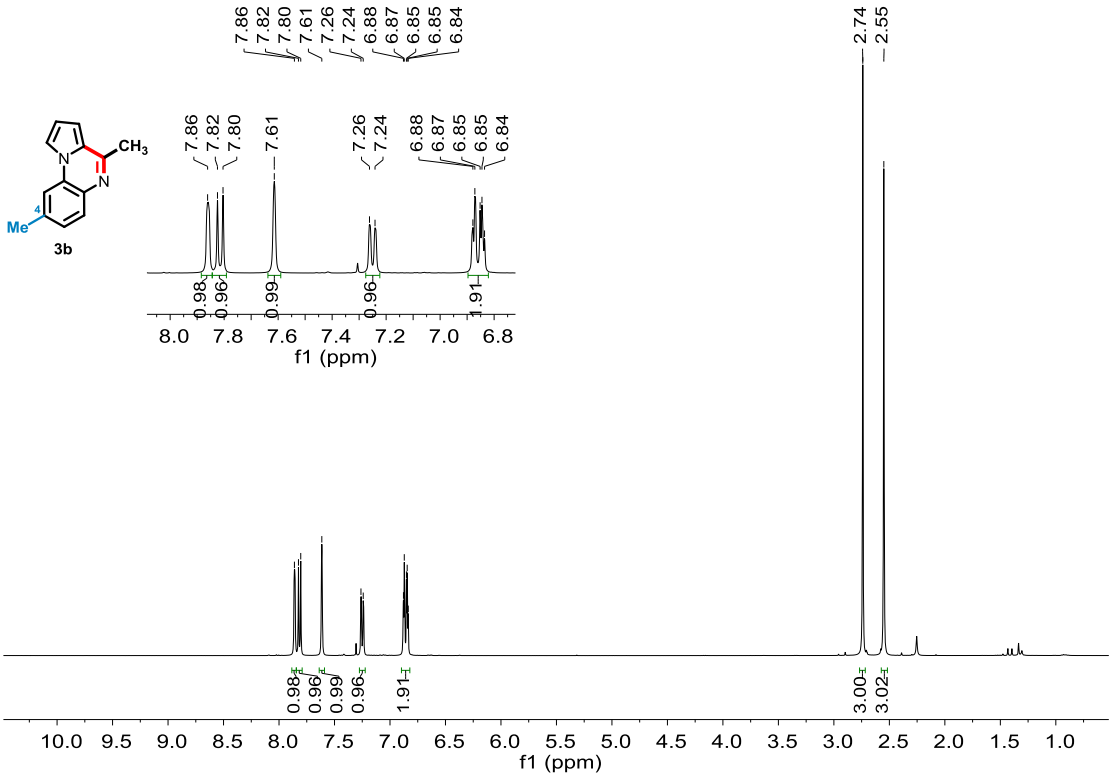
f1 (ppm)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N
Me
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3b
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0.96
0.99
0.96
1.91
3.00
3.02
8.0 7.8 7.6 7.4 7.2 7.0 6.8
f1 (ppm)
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
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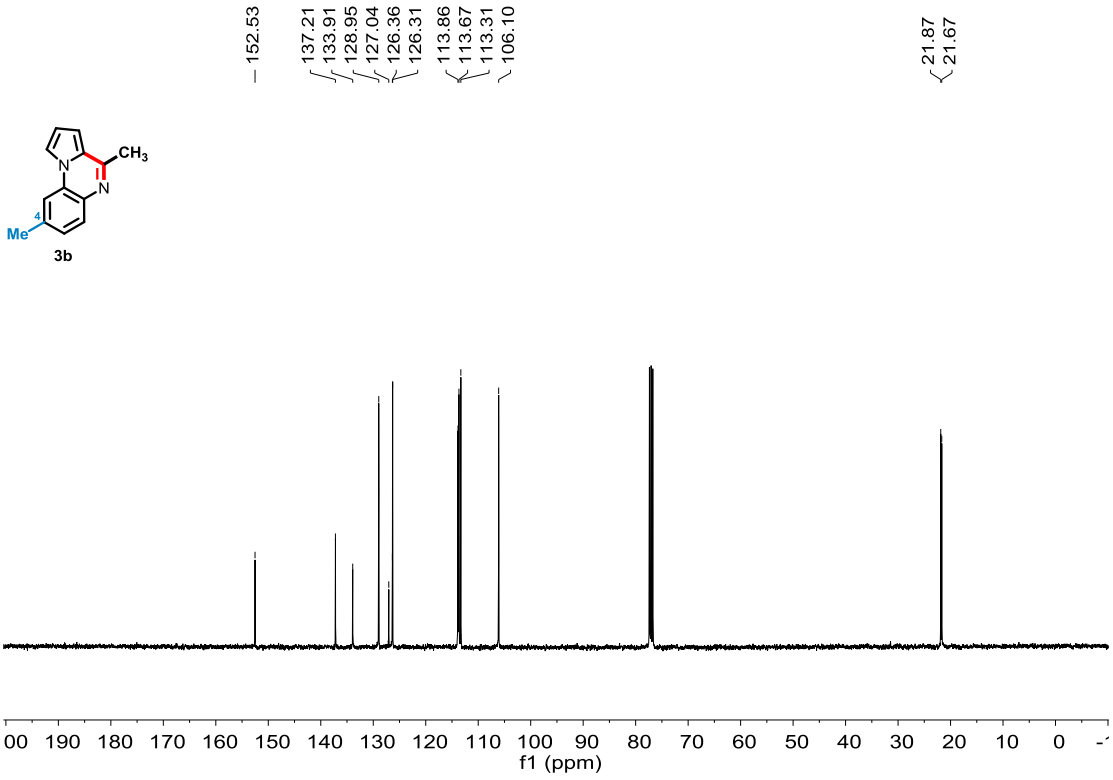
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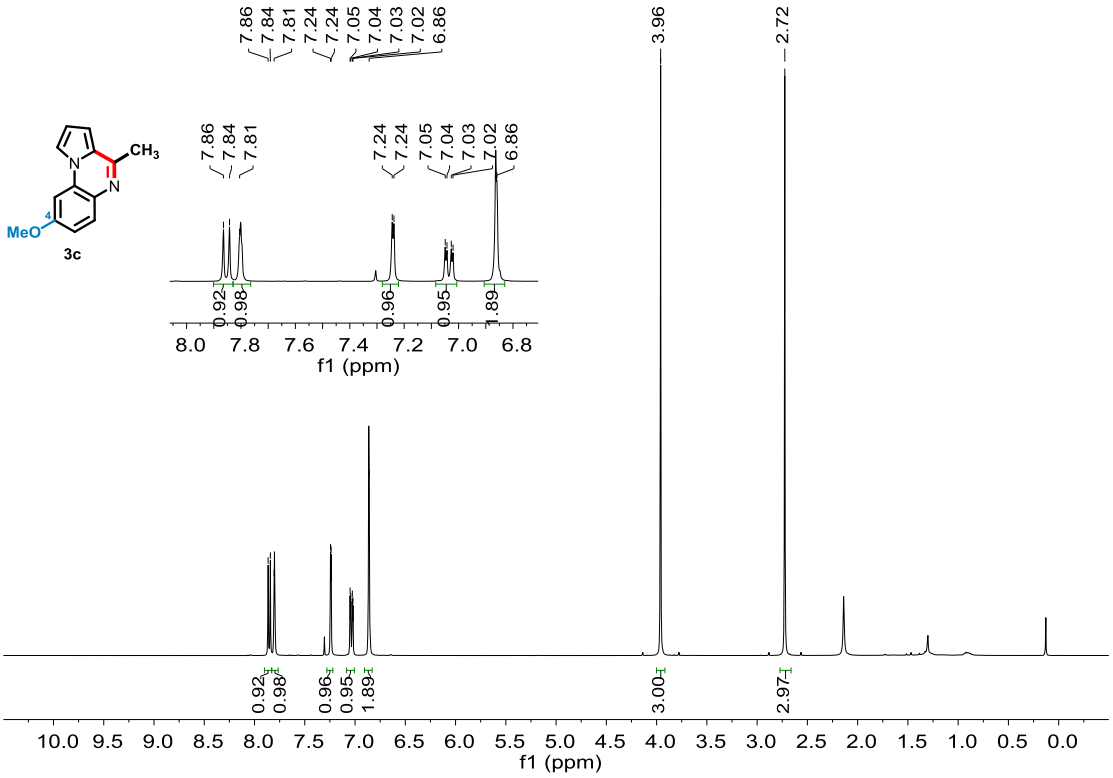
N
Me
4
3b
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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1.89
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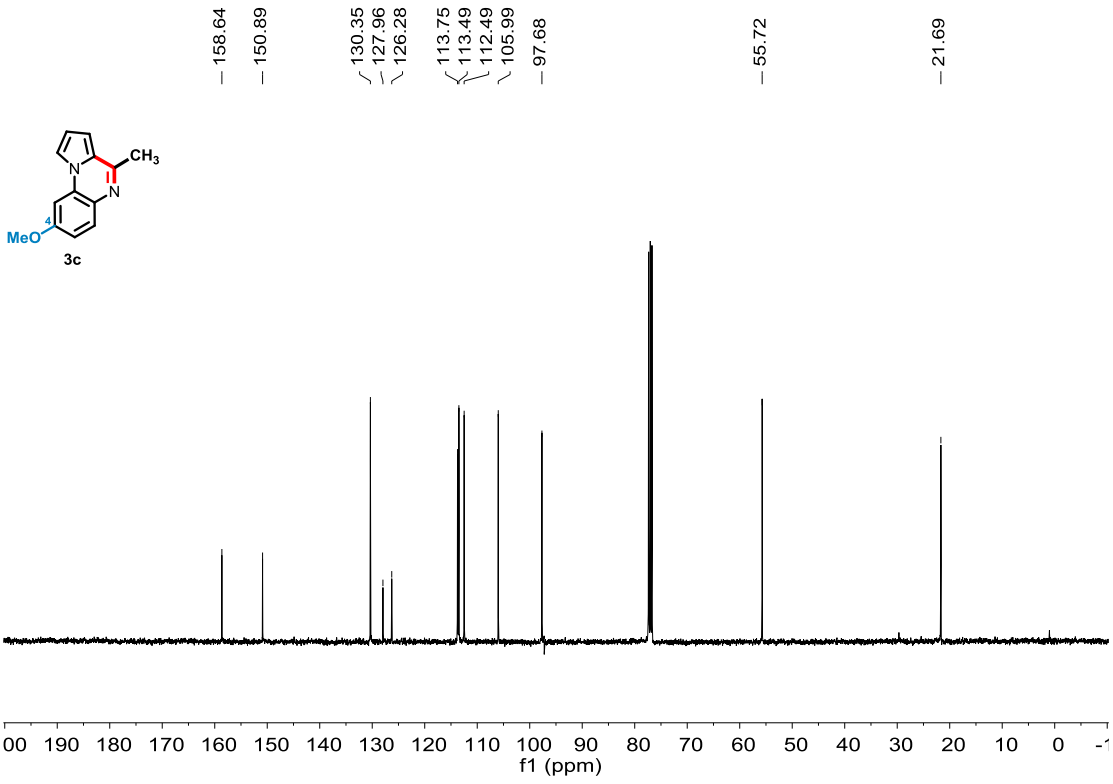
2.97
f1 (ppm)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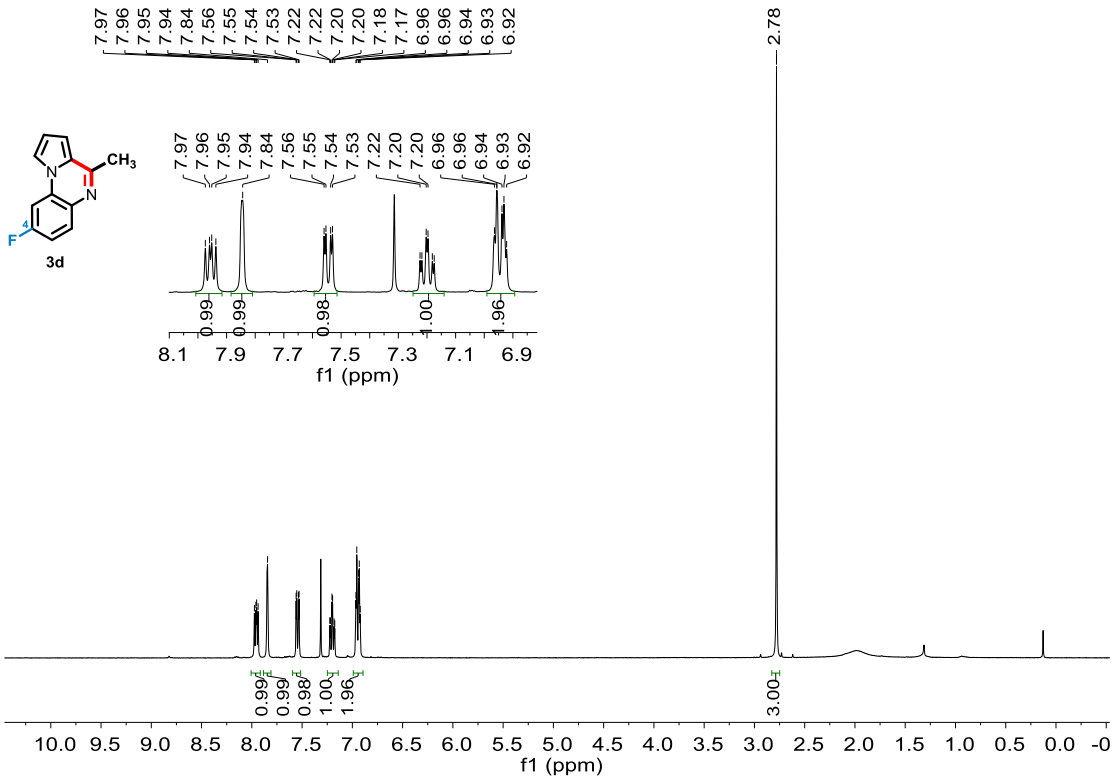
3c
f1 (ppm)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7.18
7.17
6.96
6.94
6.93
6.92
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0.99
0.98
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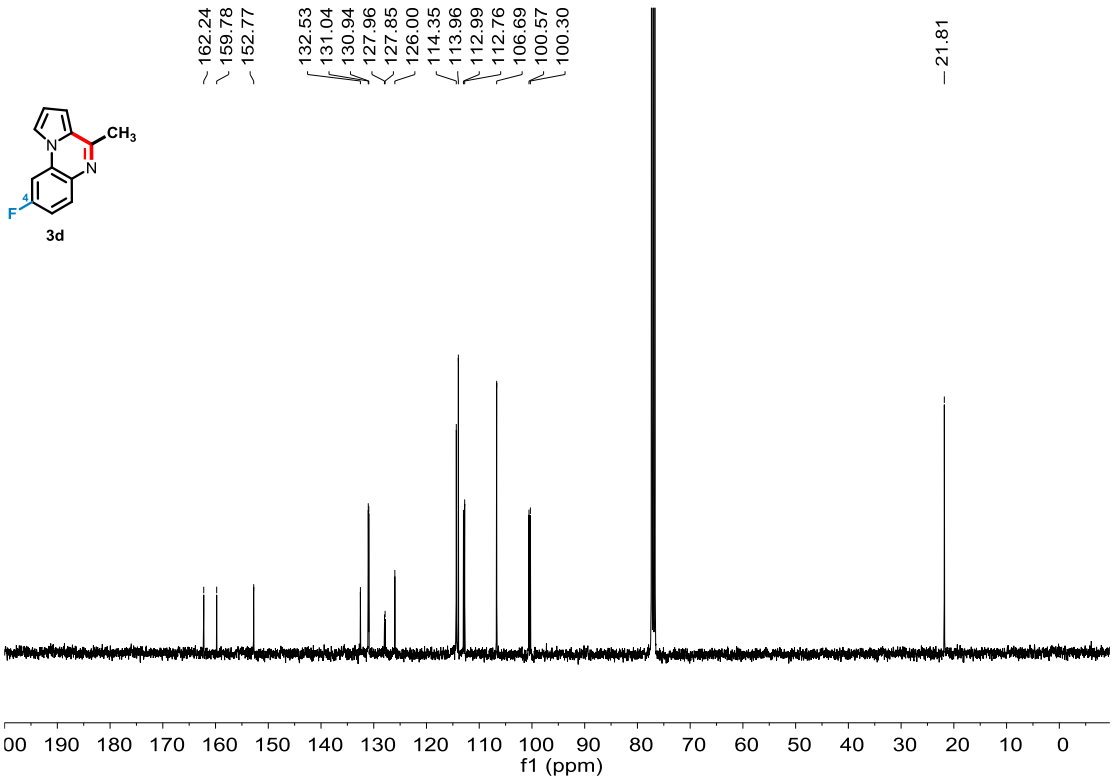
3.00
f1 (ppm)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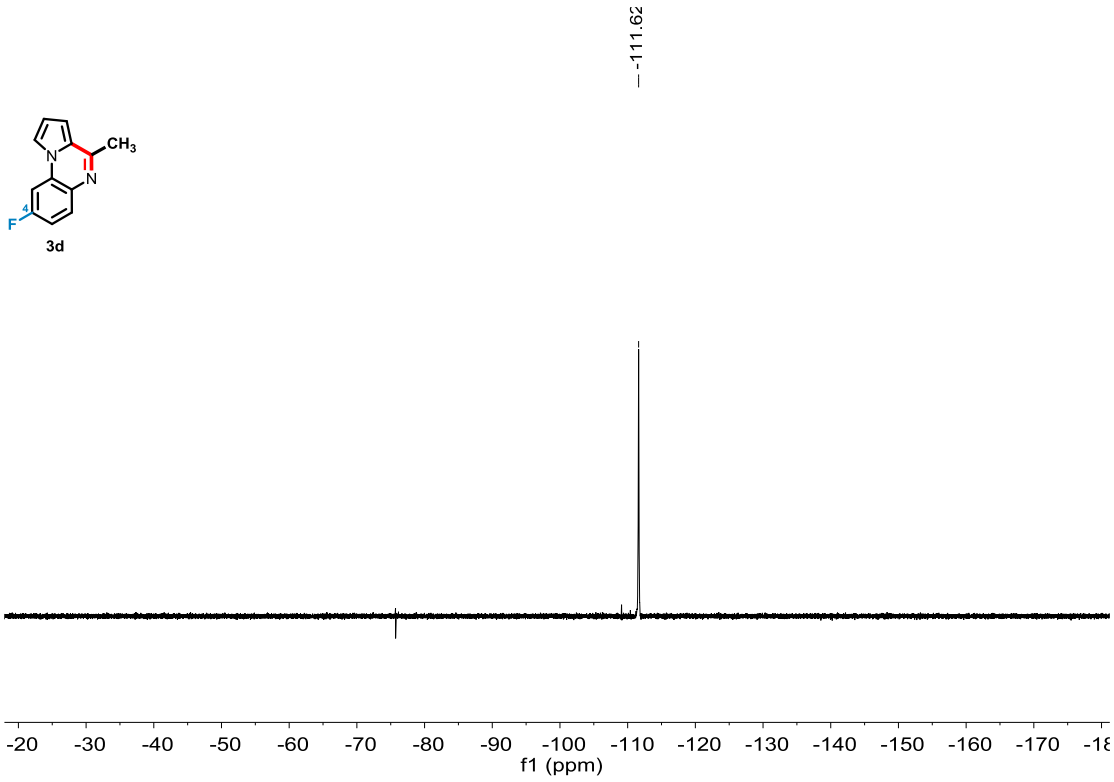
N
N
F
4
3d
f1 (ppm)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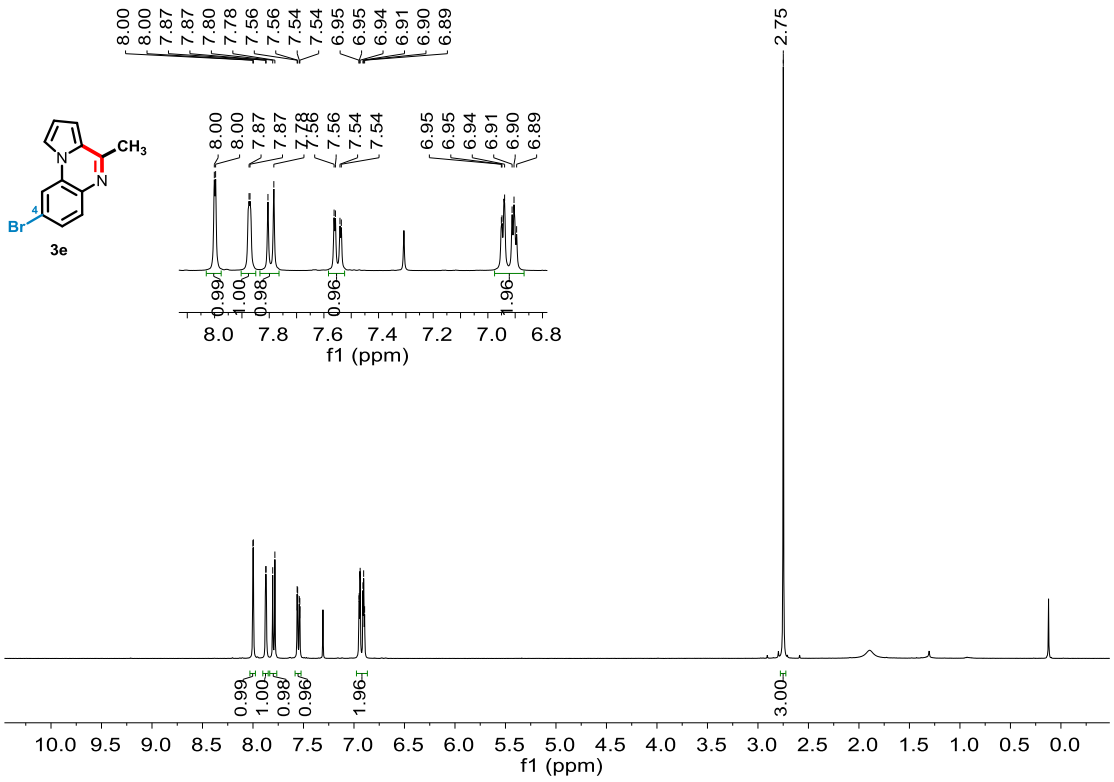
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Br
4
3e
0.99 1.00 0.98 0.96 1.96
8.0 7.8 7.6 7.4 7.2 7.0 6.8
f1 (ppm)
0.99 1.00 0.98 0.96 1.96 3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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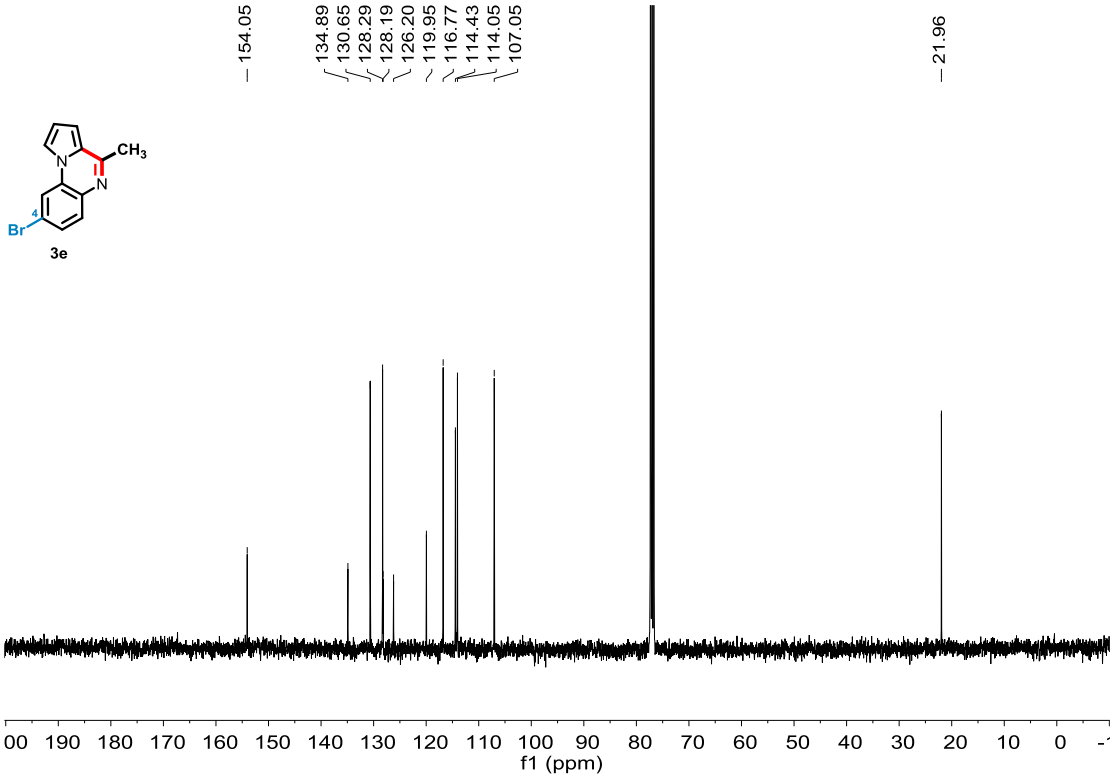
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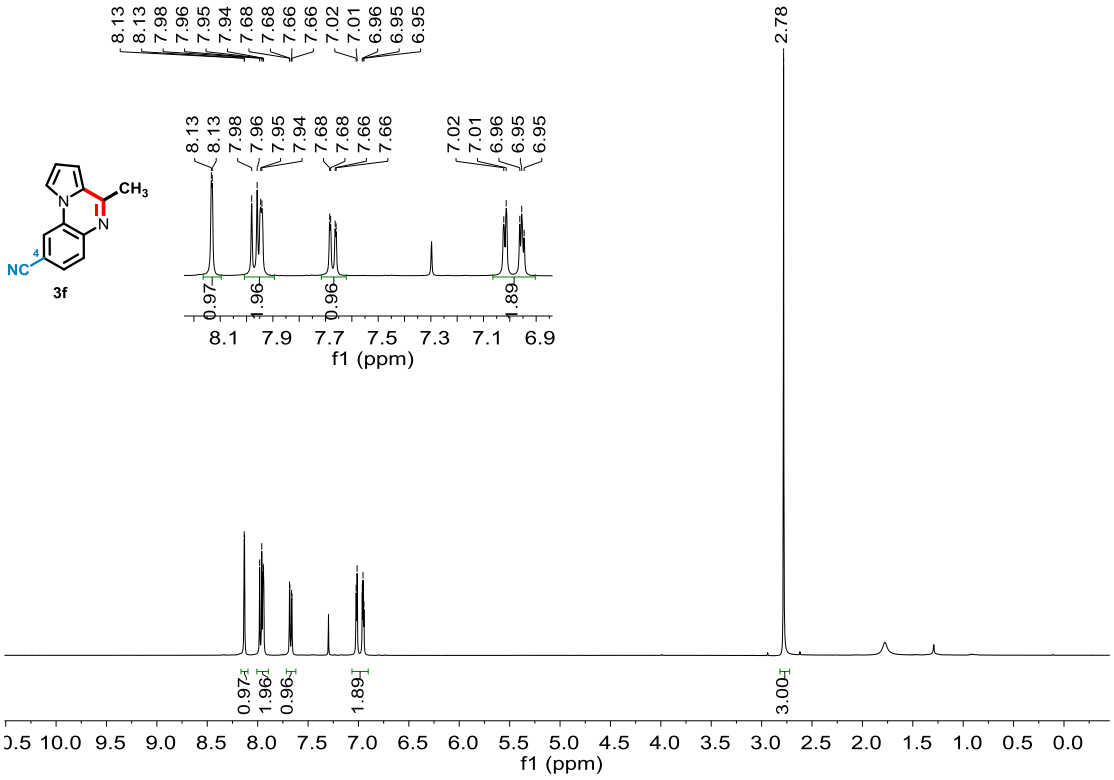
Br
4
3e
f1 (ppm)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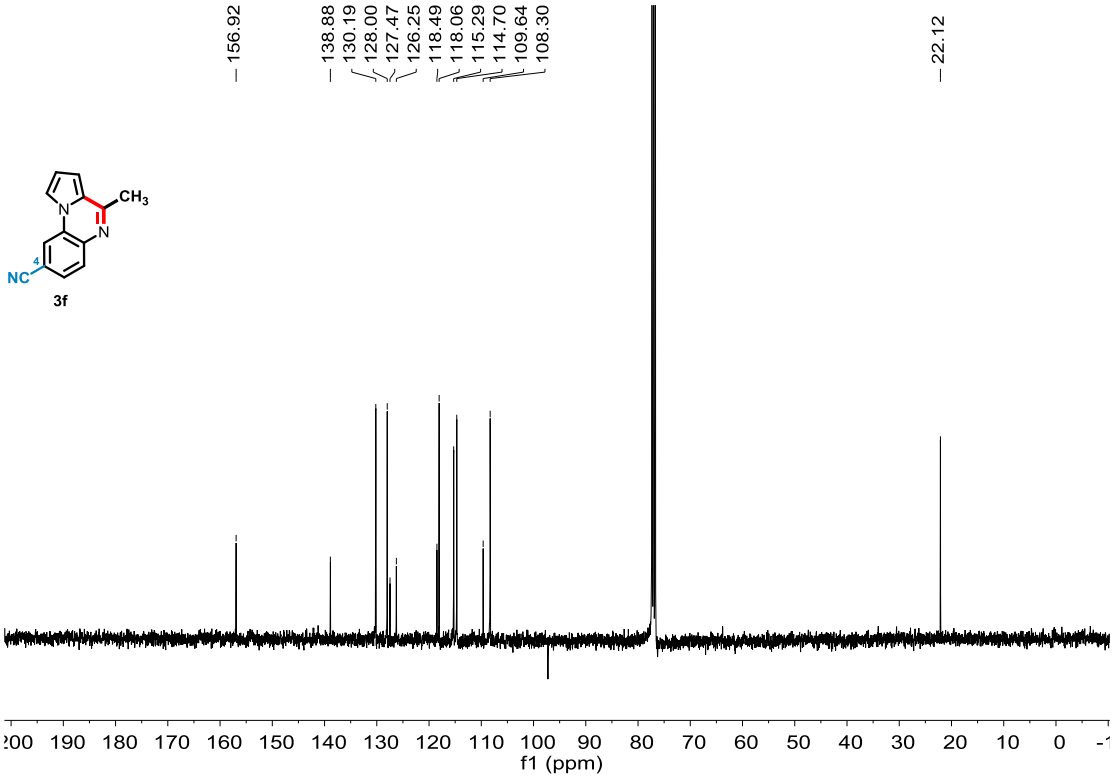
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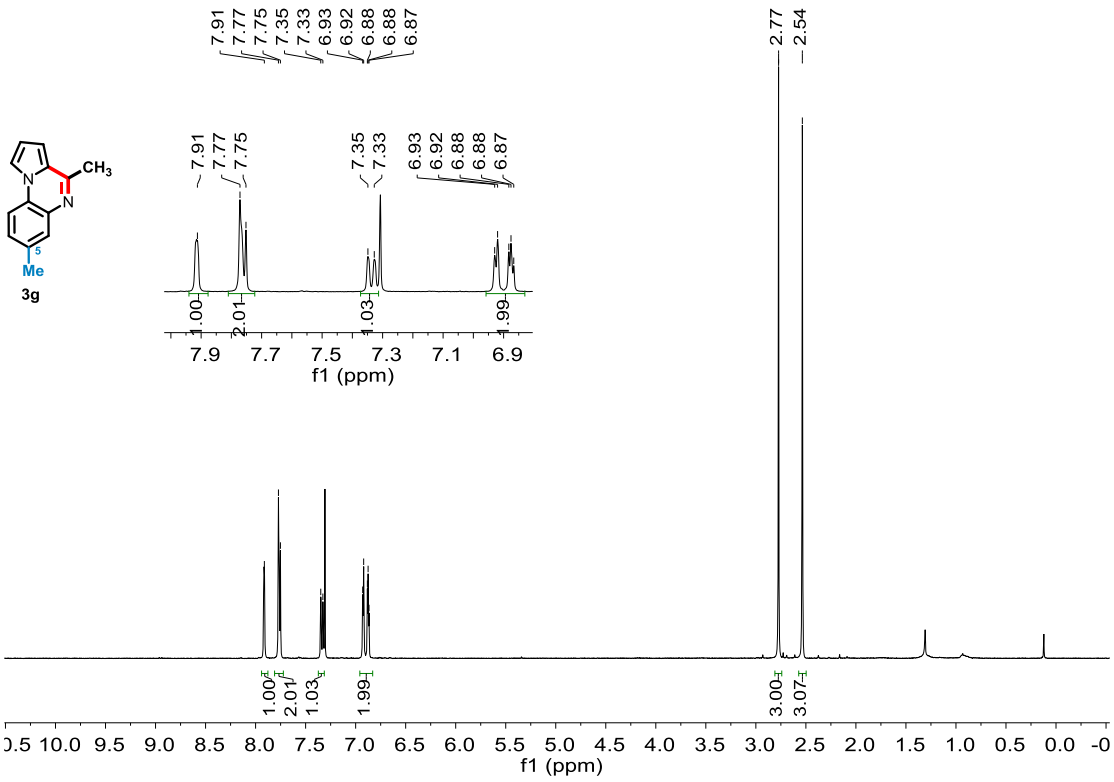
3f
f1 (ppm)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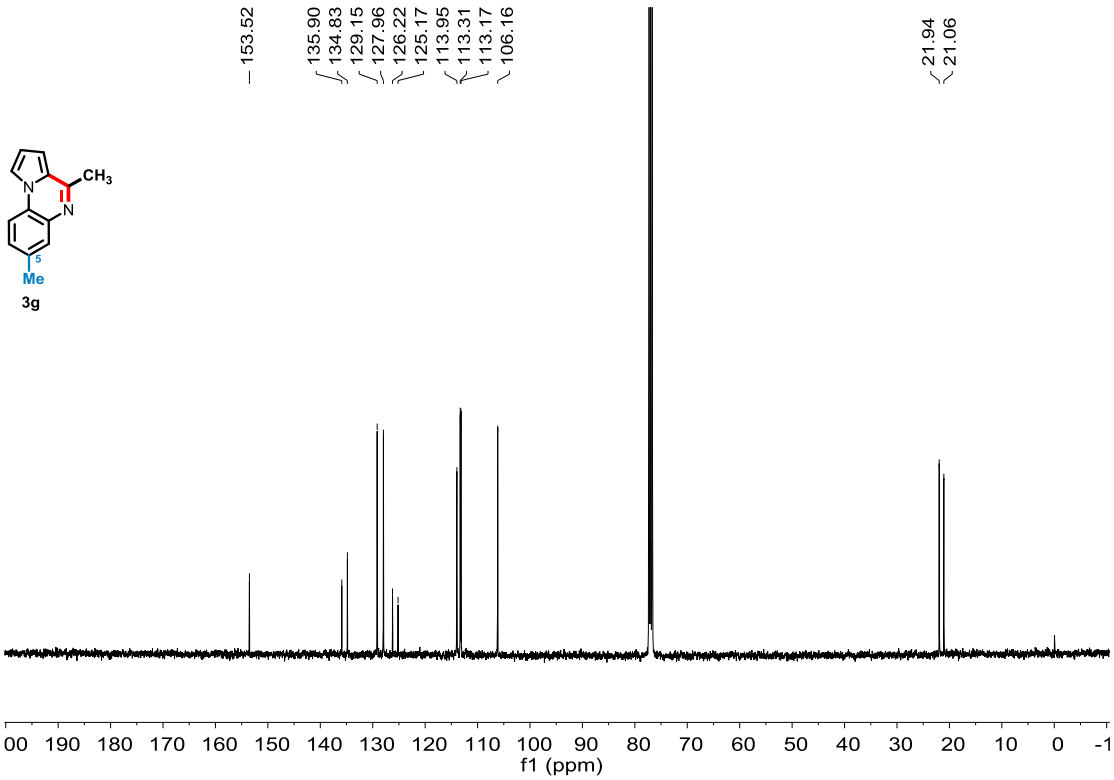
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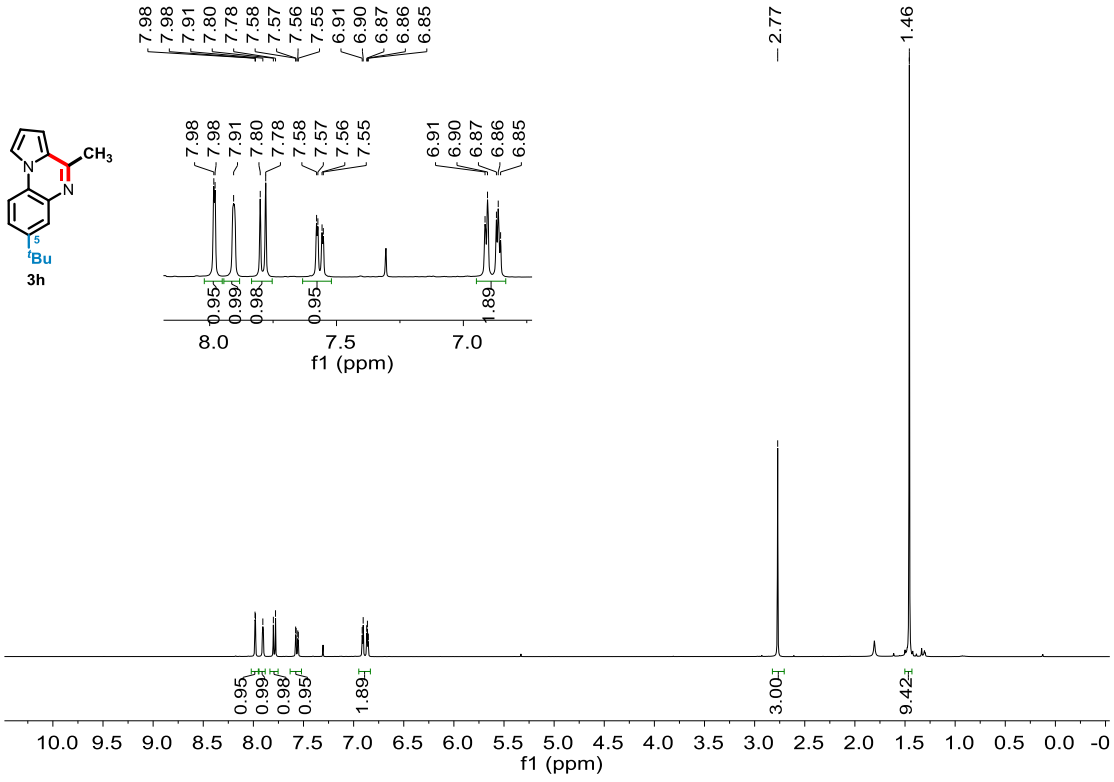
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7.5
7.0
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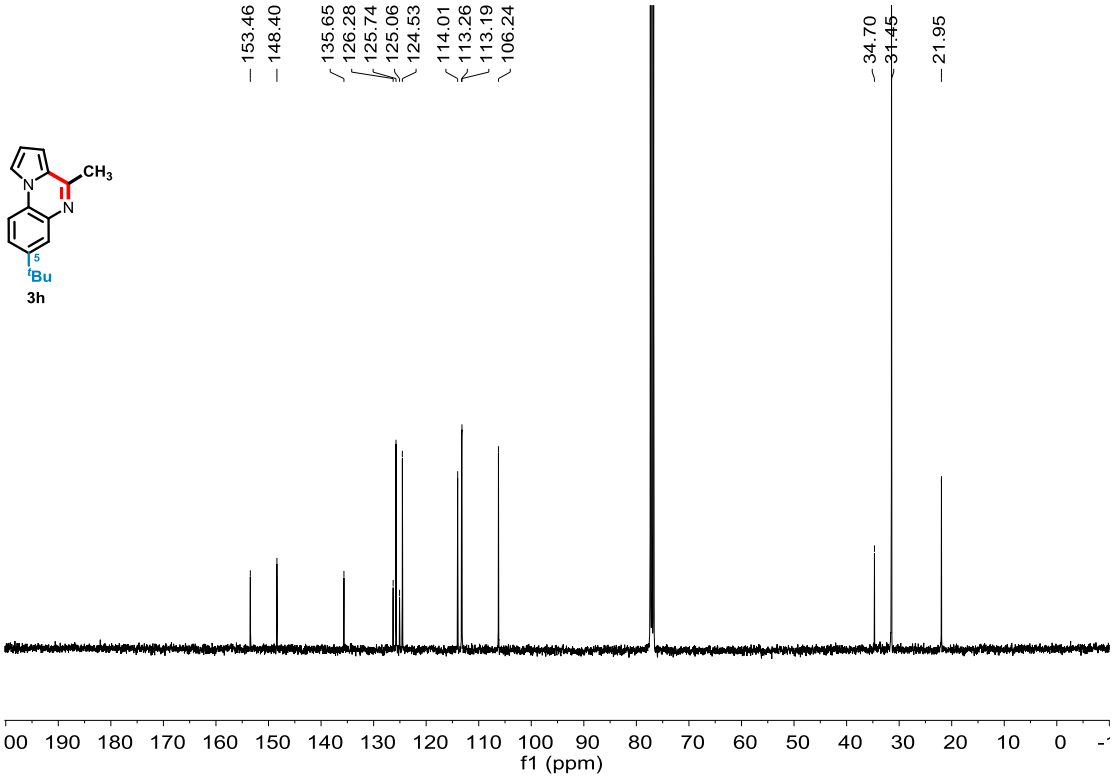
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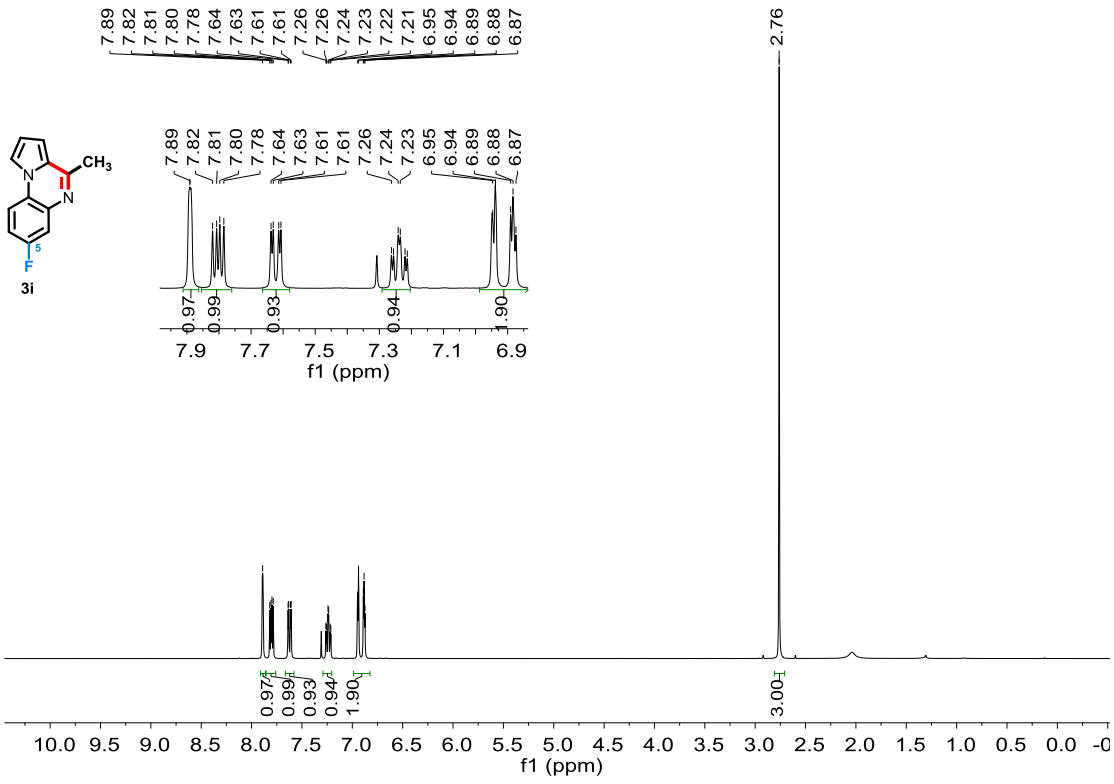
3h
f1 (ppm)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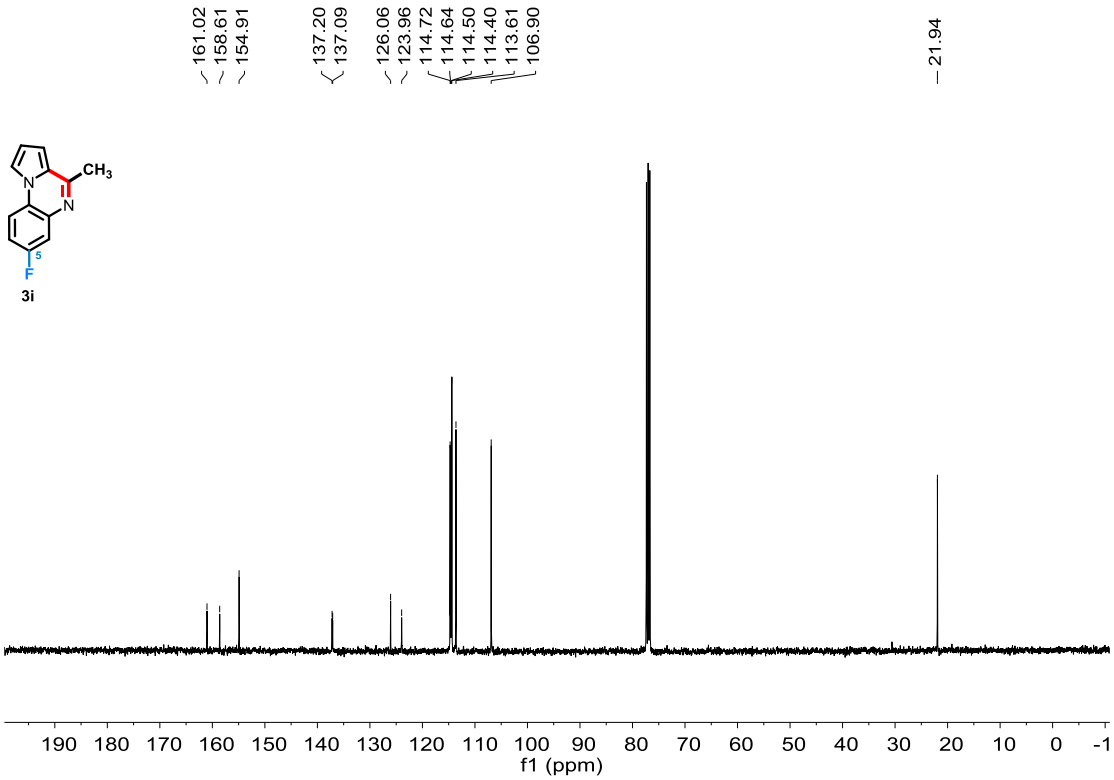
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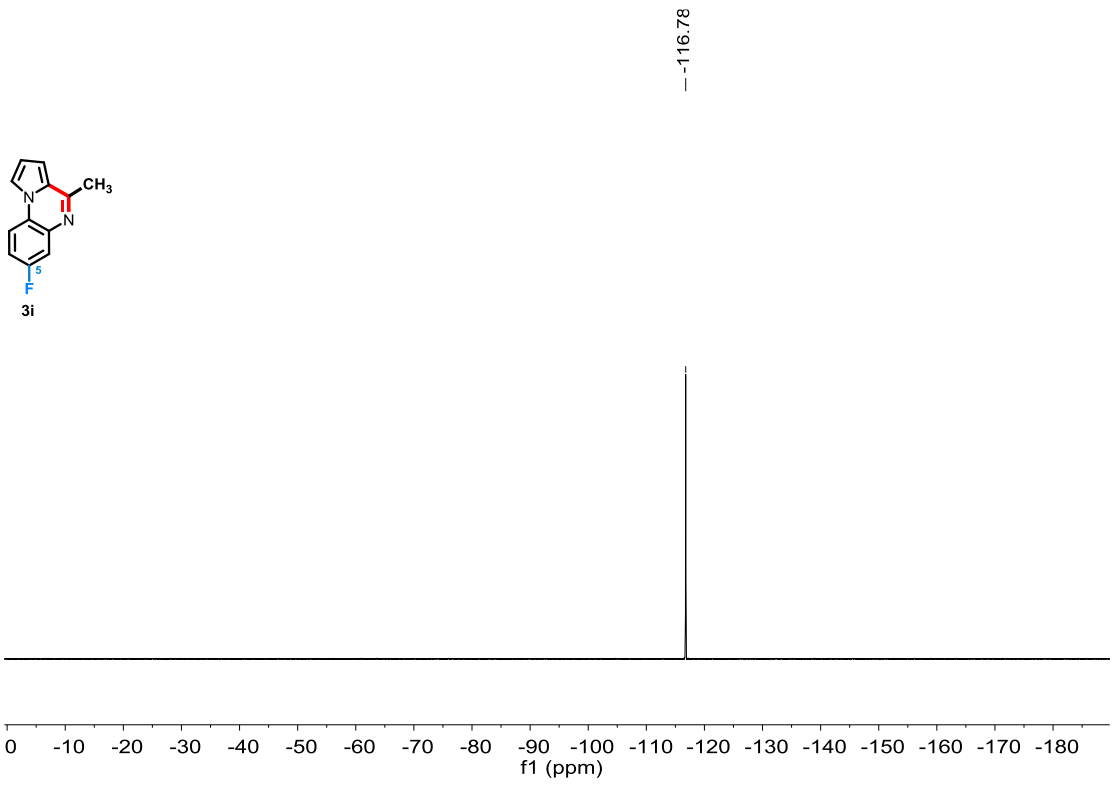
f1 (ppm)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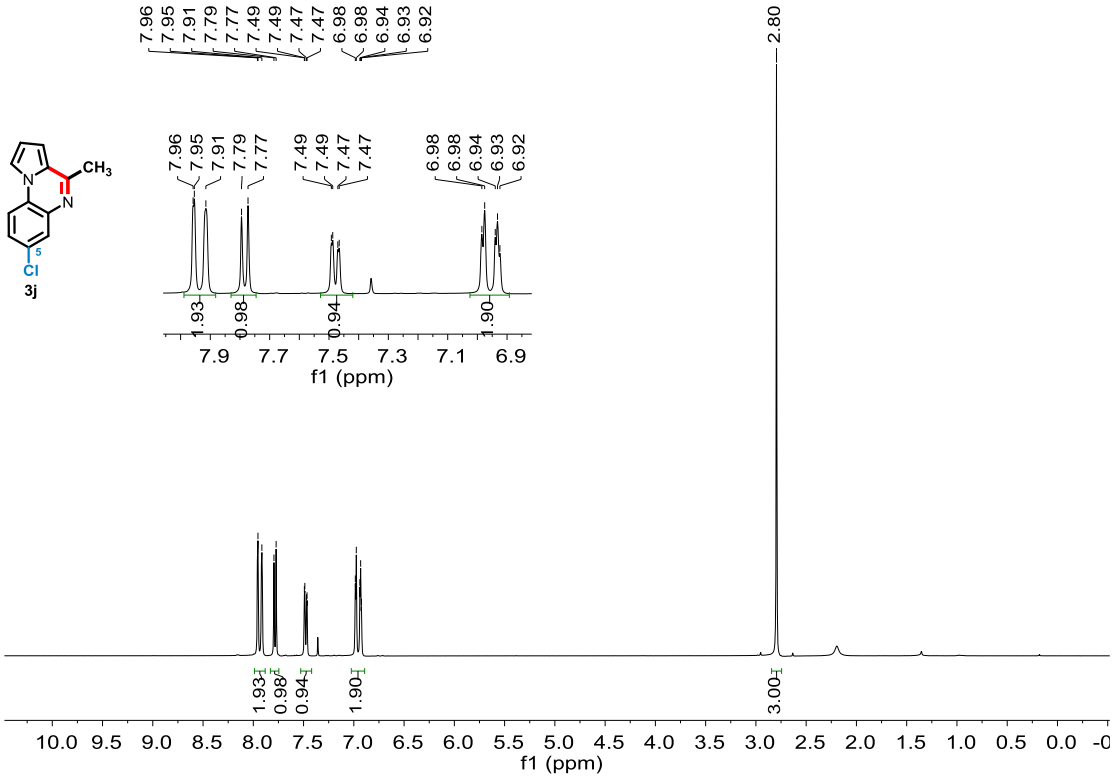
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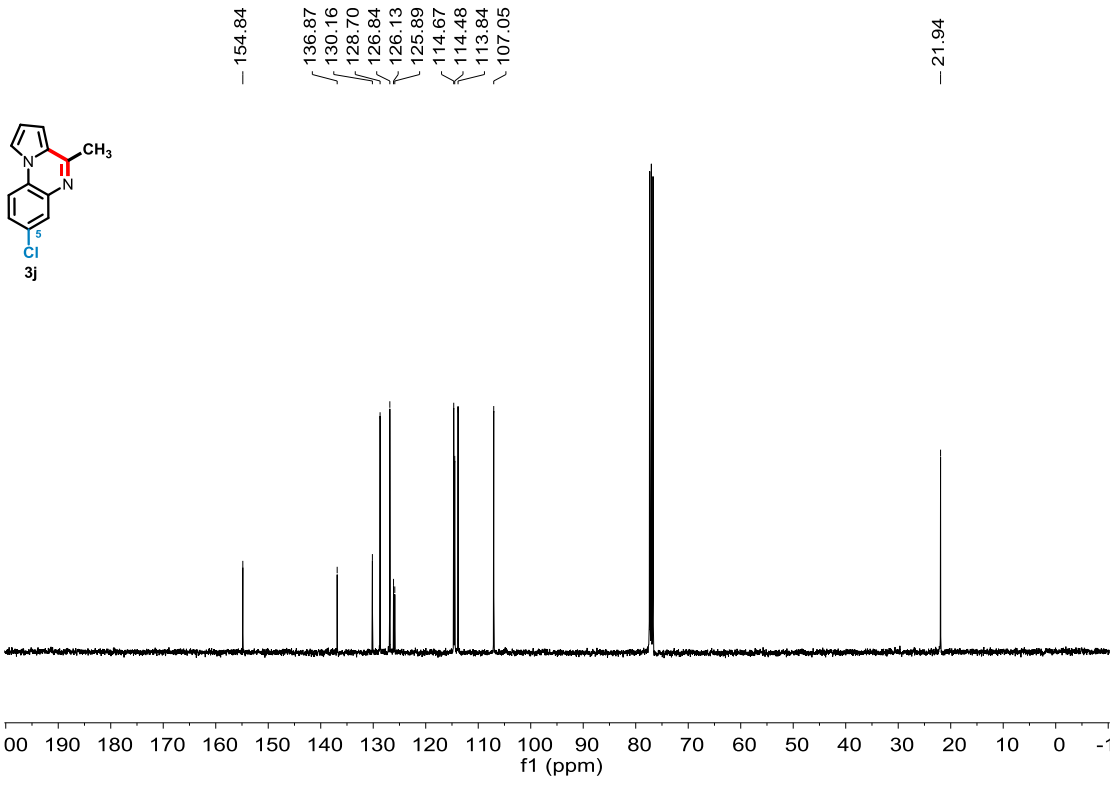
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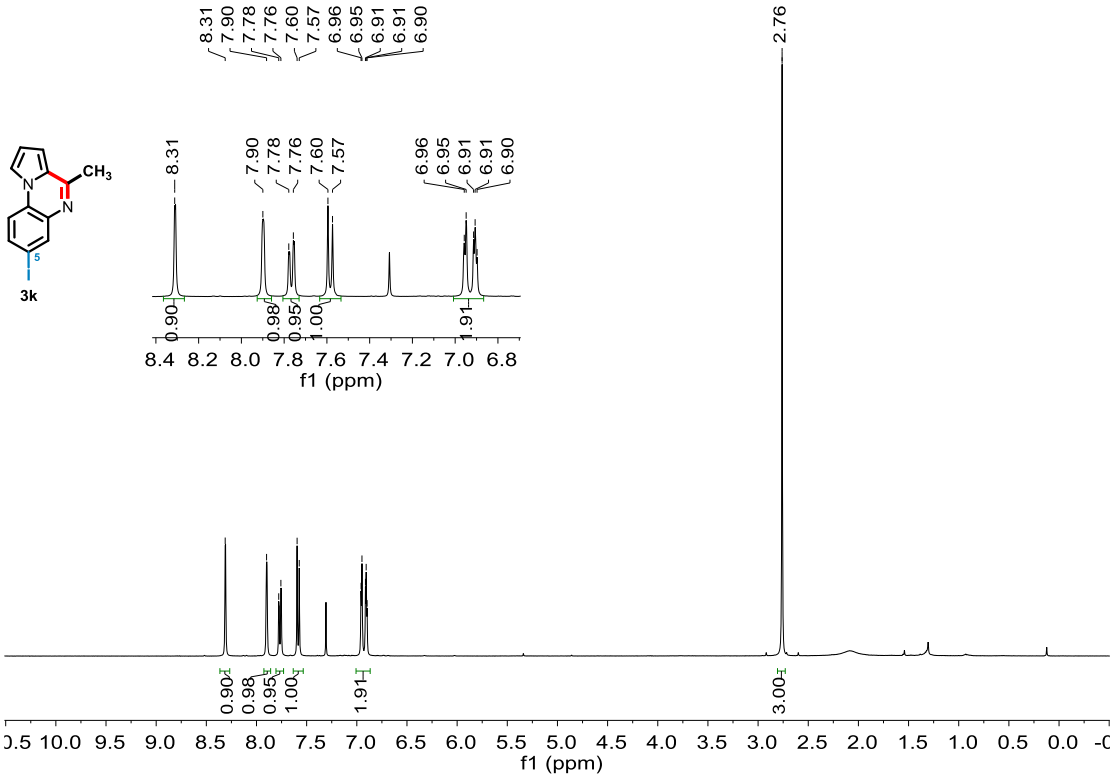
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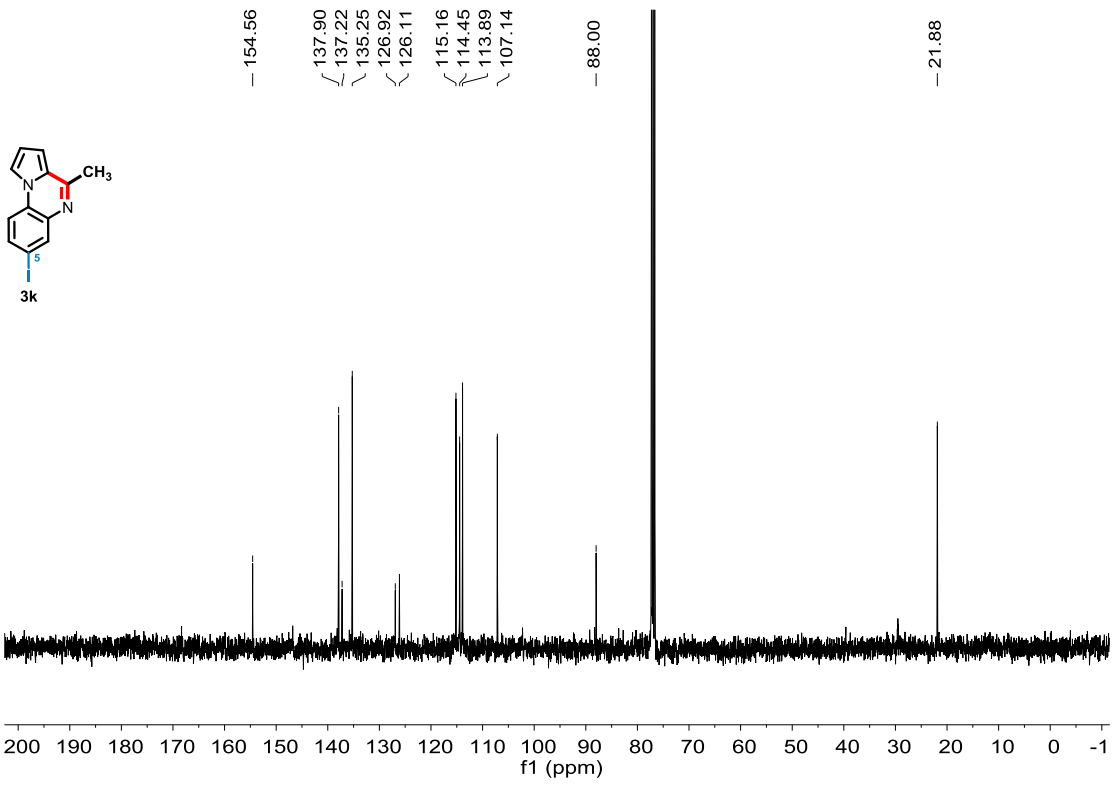
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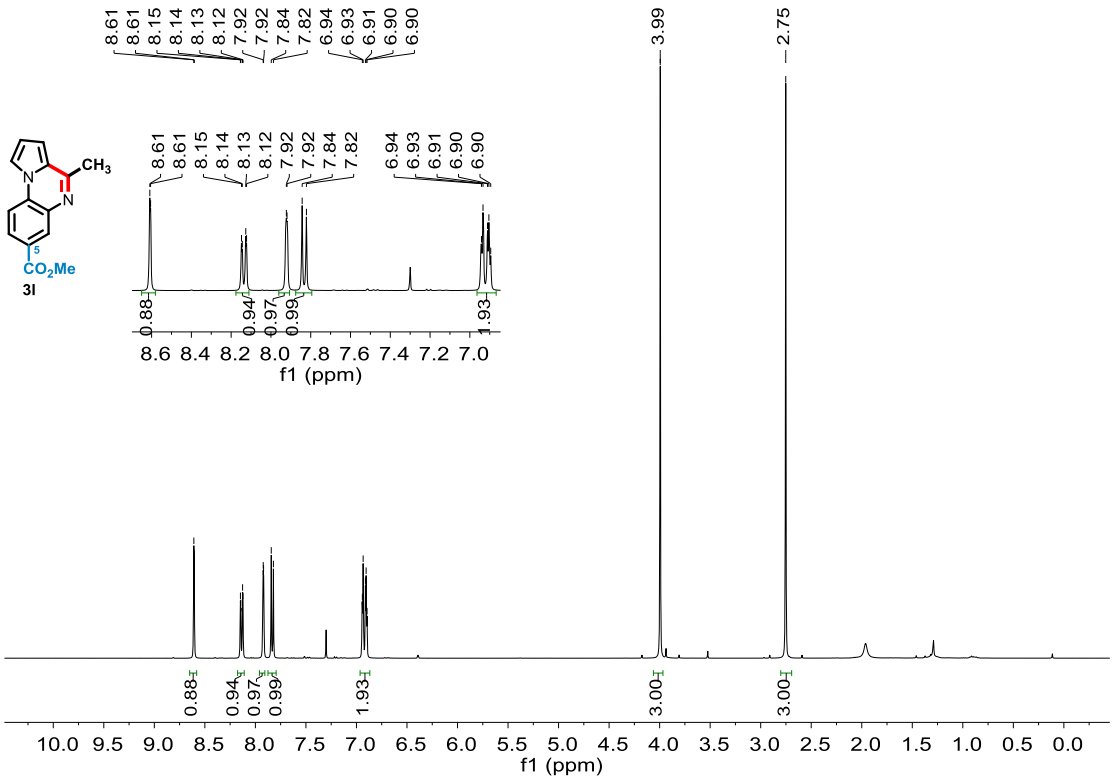
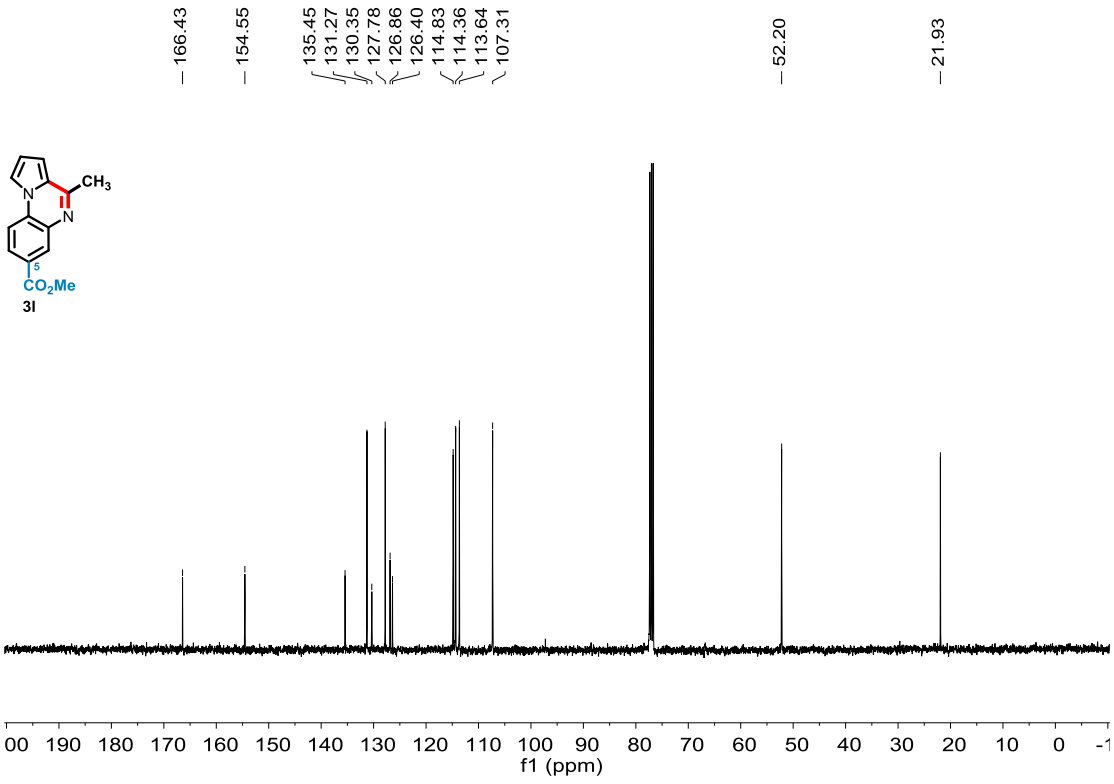
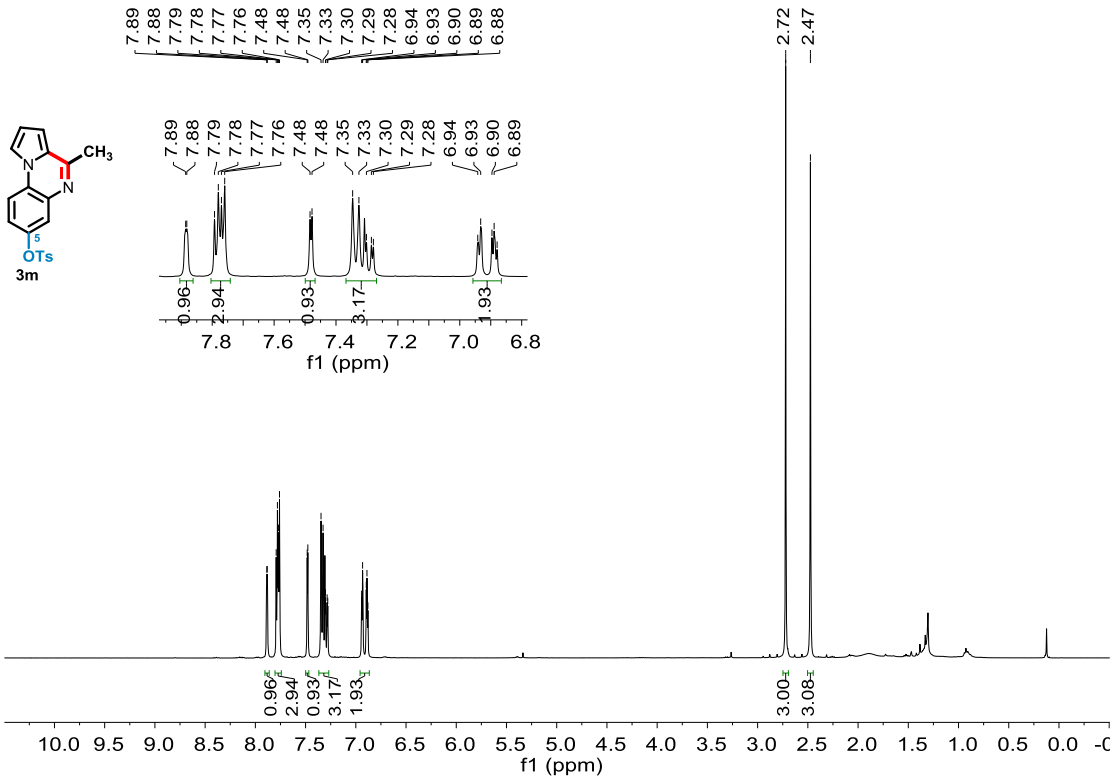
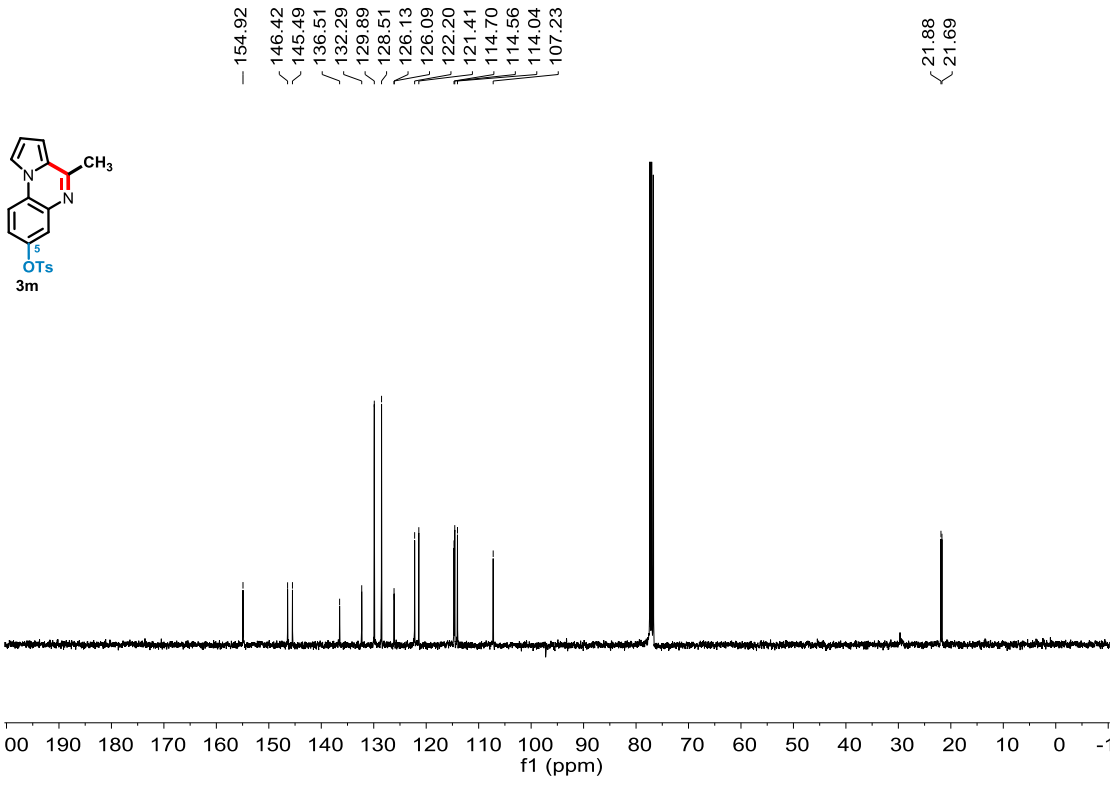
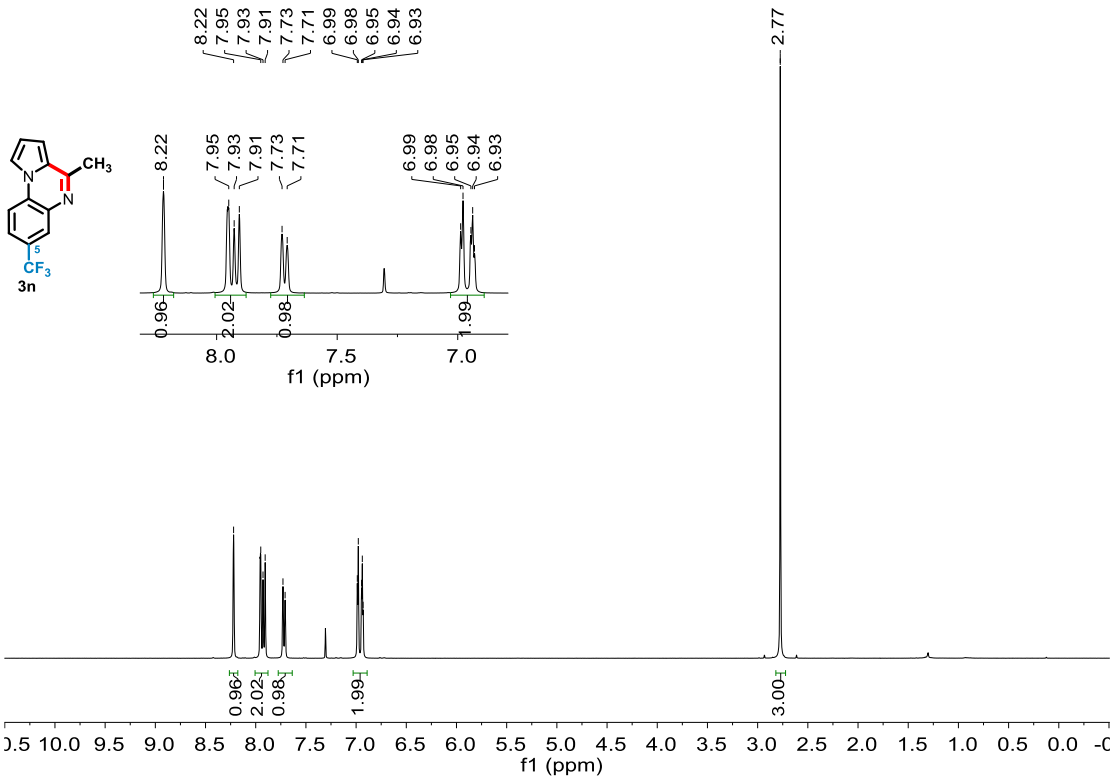
N
N
5
3k
f1 (ppm)

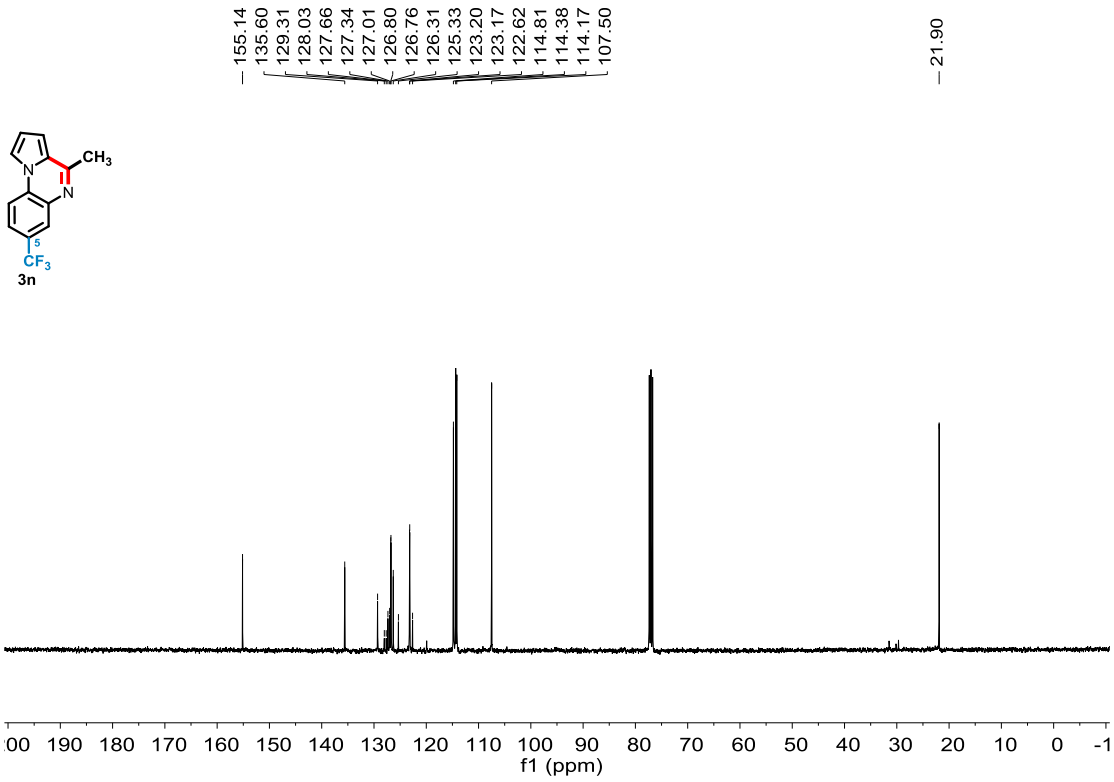

8.61
8.61
8.15
8.14
8.13
8.12
7.92
7.92
7.84
7.82
6.94
6.93
6.91
6.90
6.90
3.99
2.75
CH3
N
N
5
CO2Me
3l
0.88
0.94
0.97
0.99
1.93
3.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0
f1 (ppm)

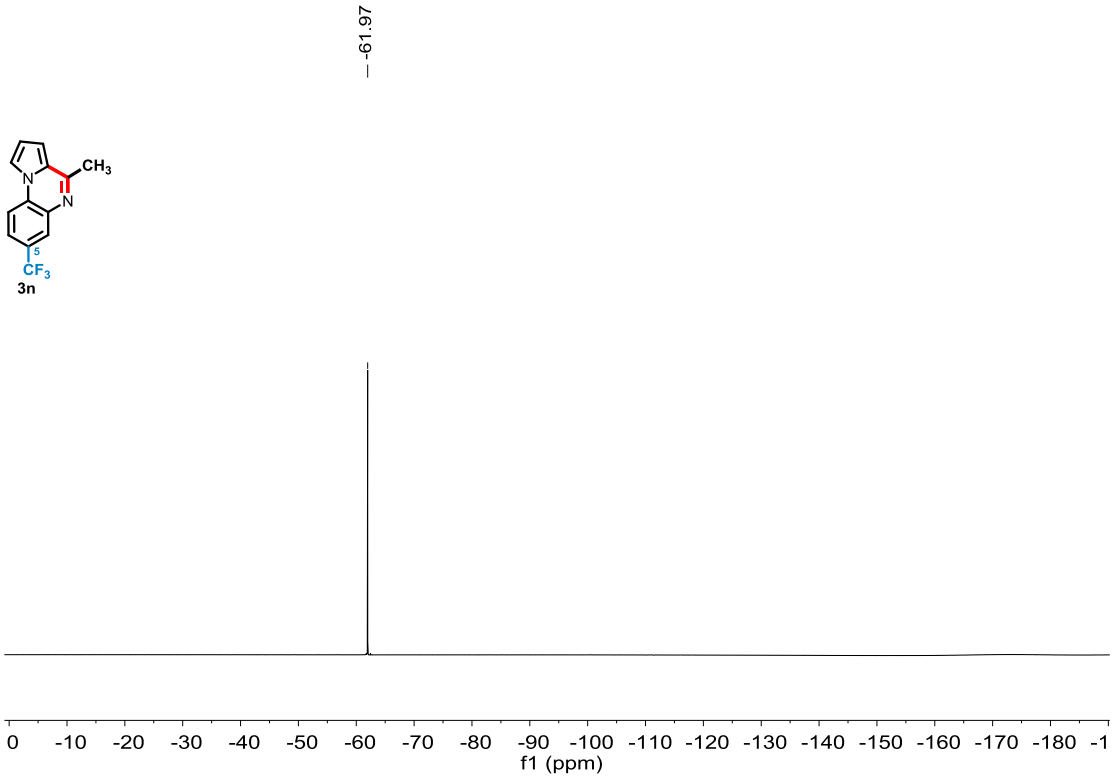

166.43
154.55
135.45
131.27
130.35
127.78
126.86
126.40
114.83
114.36
113.64
107.31
52.20
21.93
CH3
N
N
5
CO2Me
3l
f1 (ppm)

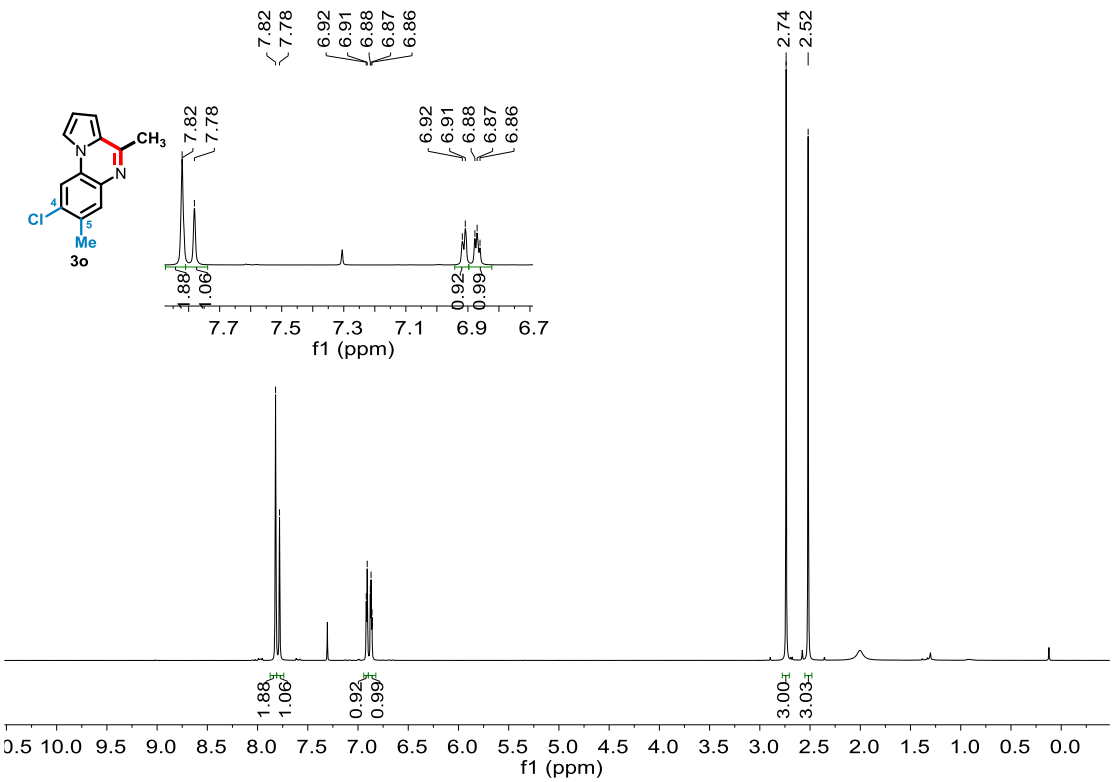

7.89
7.88
7.79
7.78
7.77
7.76
7.48
7.48
7.35
7.33
7.30
7.29
7.28
6.94
6.93
6.90
6.89
6.88
2.72
2.47
CH3
N
N
5
OTs
3m
0.96
2.94
0.93
3.17
1.93
3.00
3.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
7.8 7.6 7.4 7.2 7.0 6.8
f1 (ppm)

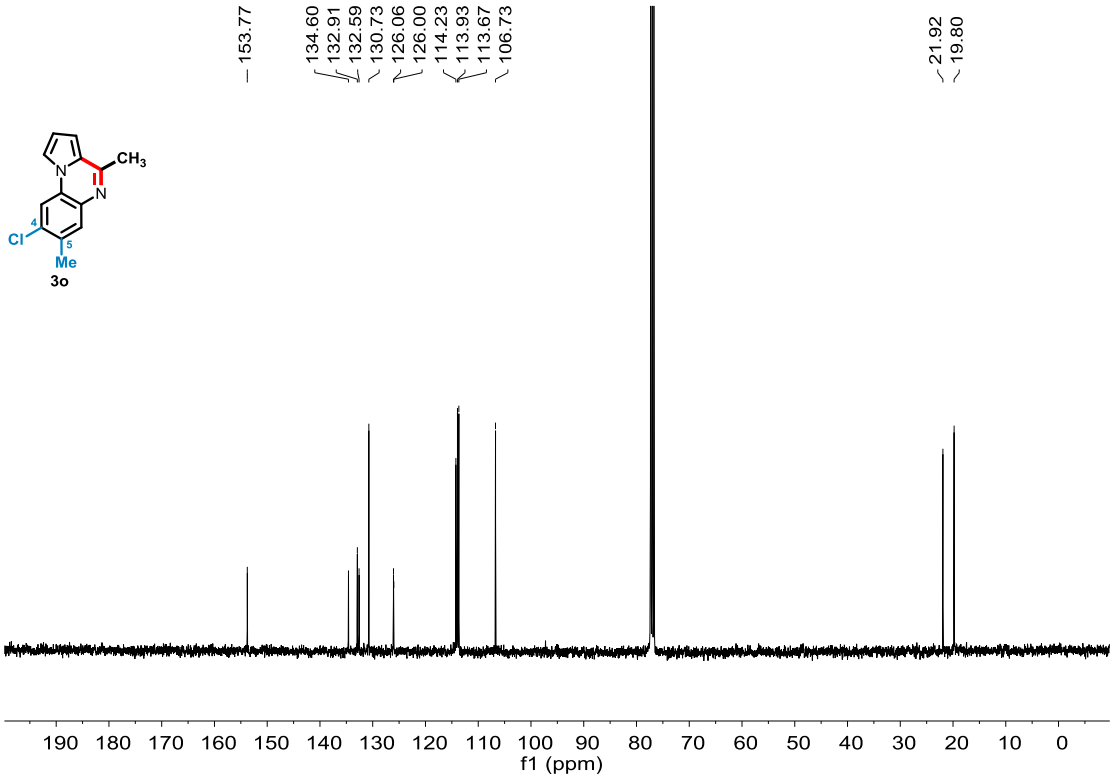

154.92
146.42
145.49
136.51
132.29
129.89
128.51
126.13
126.09
122.20
121.41
114.70
114.56
114.04
107.23
21.88
21.69
CH3
N
N
5
OTs
3m
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

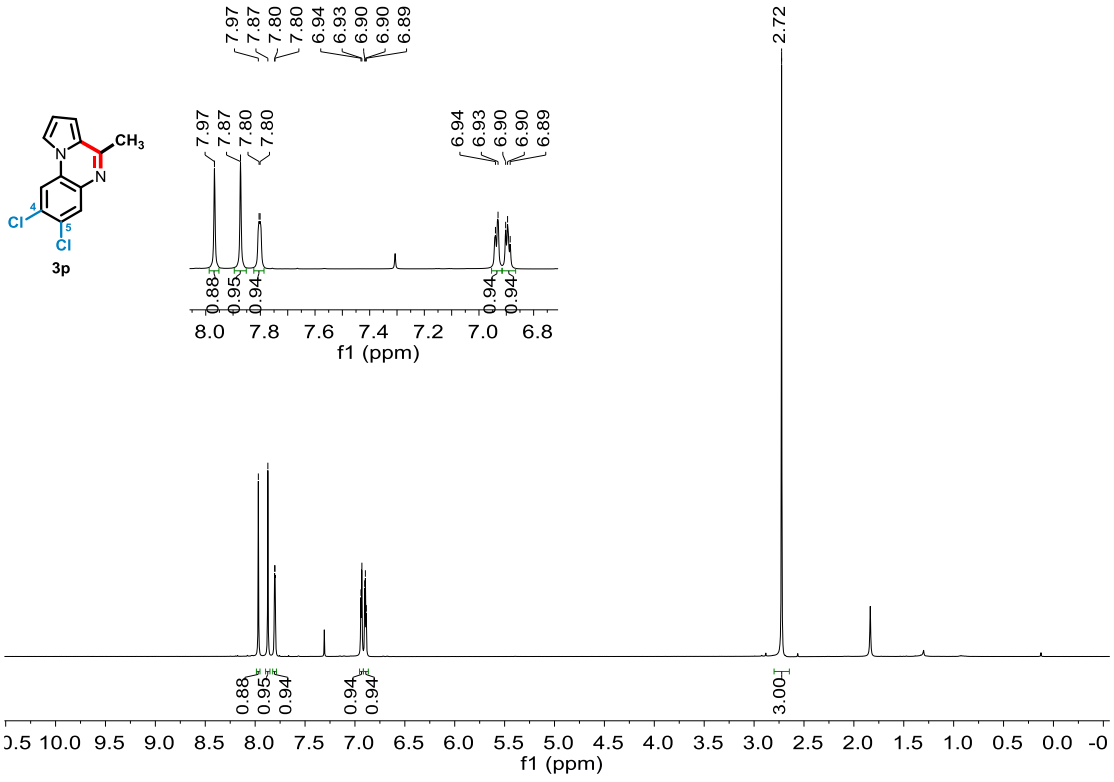

8.22
7.95
7.93
7.91
7.73
7.71
6.99
6.98
6.95
6.94
6.93
2.77
CH3
N
N
CF3
5
3n
0.96
2.02
0.98
1.99
3.00
f1 (ppm)

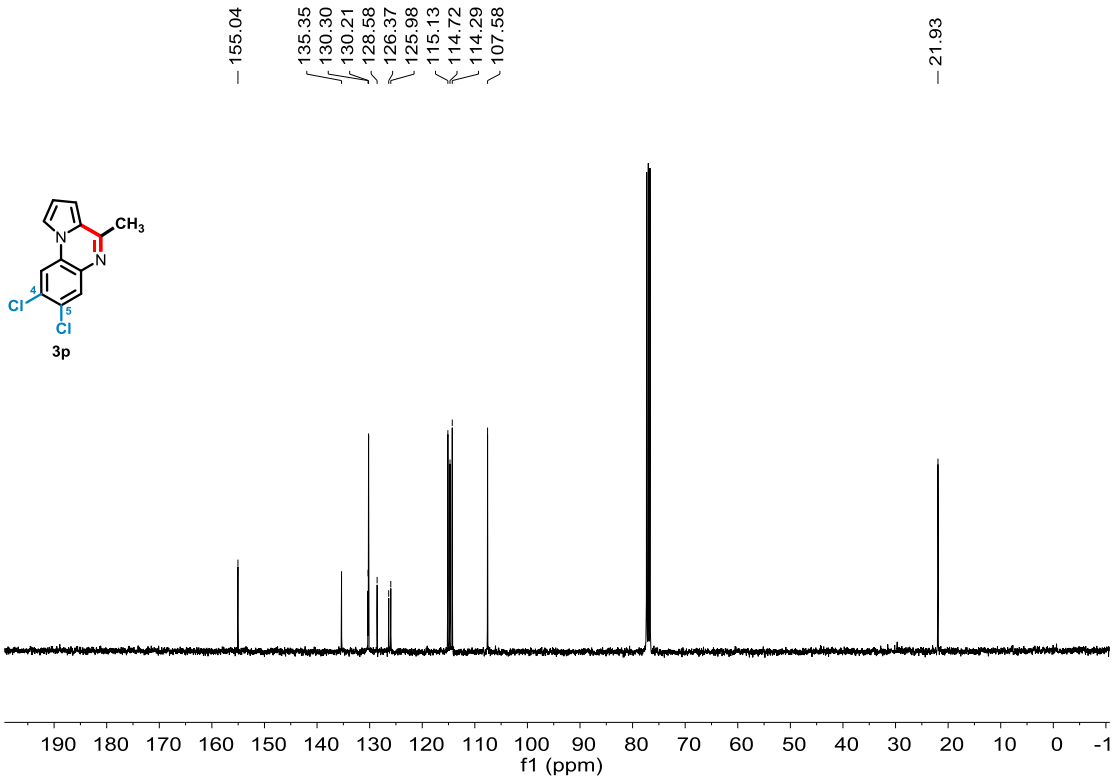

155.14
135.60
129.31
128.03
127.66
127.34
127.01
126.80
126.76
126.31
125.33
123.20
123.17
122.62
114.81
114.38
114.17
107.50
21.90
CH3
N
N
CF3
5
3n
f1 (ppm)

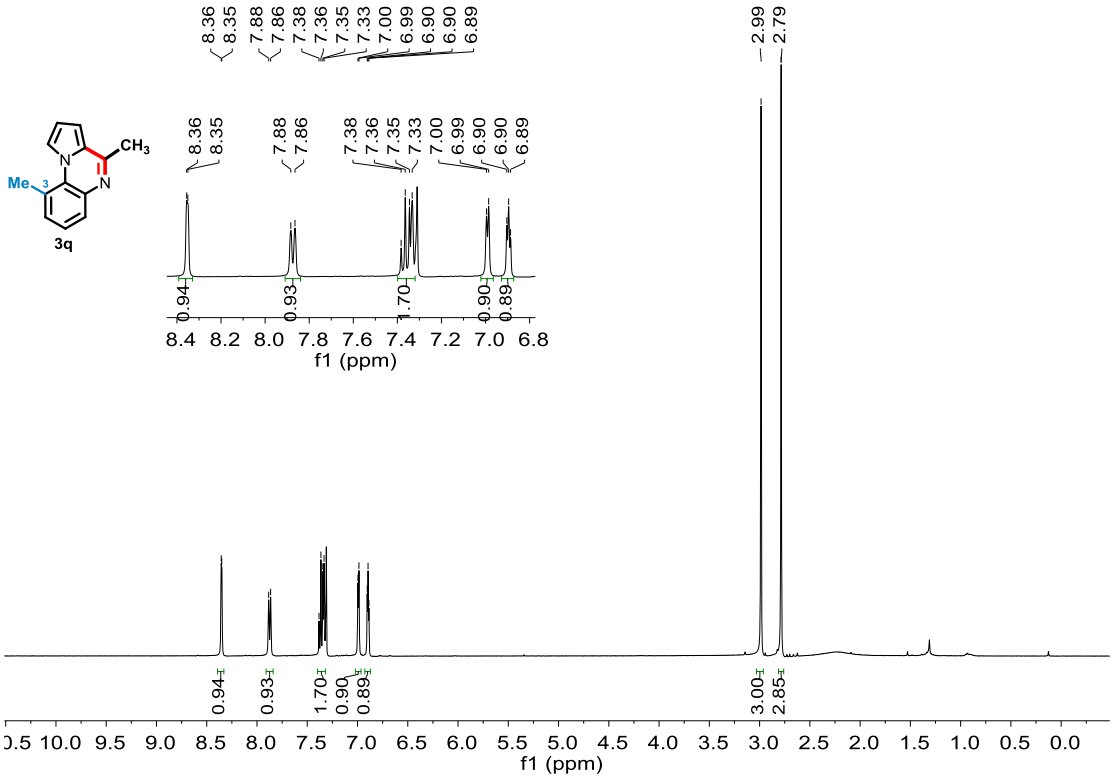

-61.97
CH3
N
N
5
CF3
3n
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -1
f1 (ppm)

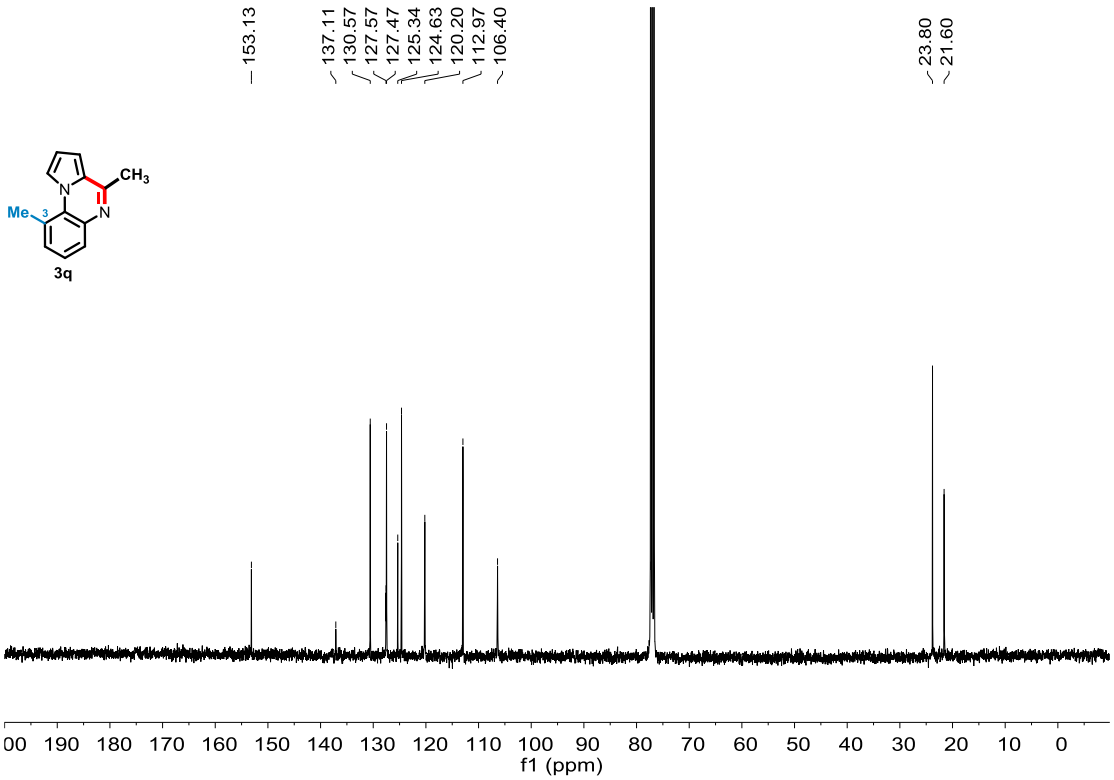

7.82
7.78
6.92
6.91
6.88
6.87
6.86
2.74
2.52
CH3
N
N
Cl
4
5
Me
3o
1.88
1.06
0.92
0.99
7.7 7.5 7.3 7.1 6.9 6.7
f1 (ppm)
1.88
1.06
0.92
0.99
3.00
3.03
0.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

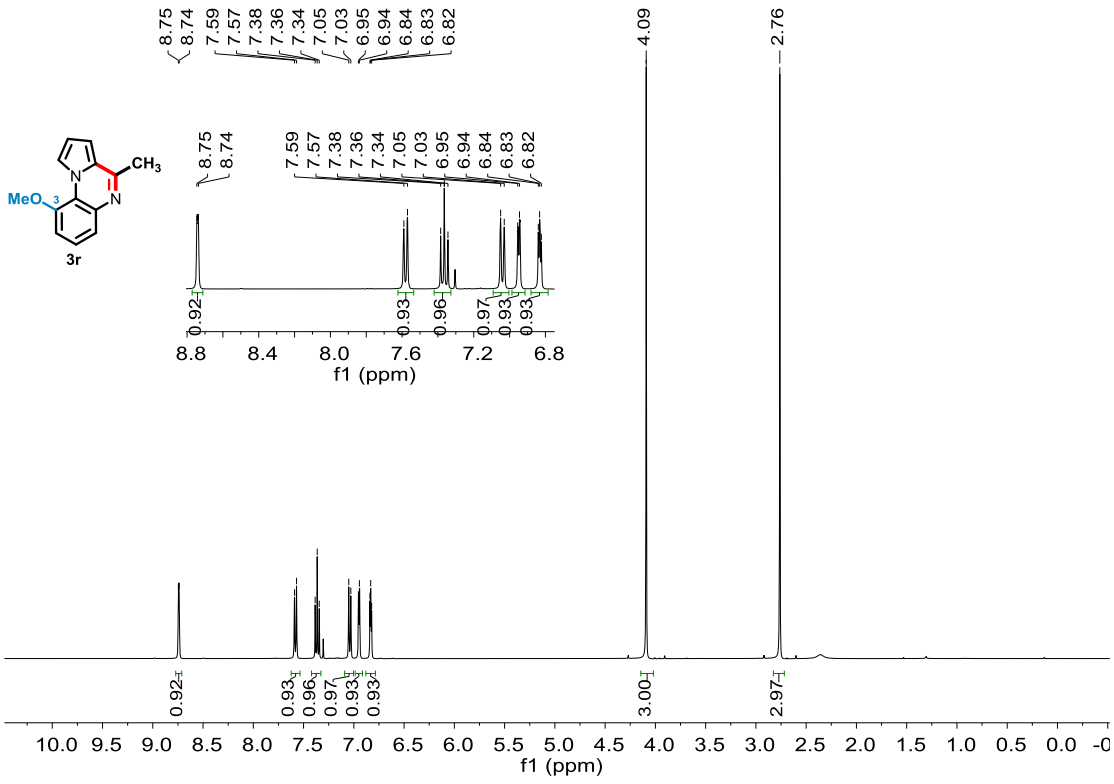

153.77
134.60
132.91
132.59
130.73
126.06
126.00
114.23
113.93
113.67
106.73
21.92
19.80
CH3
N
N
Cl
4
5
Me
3o
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

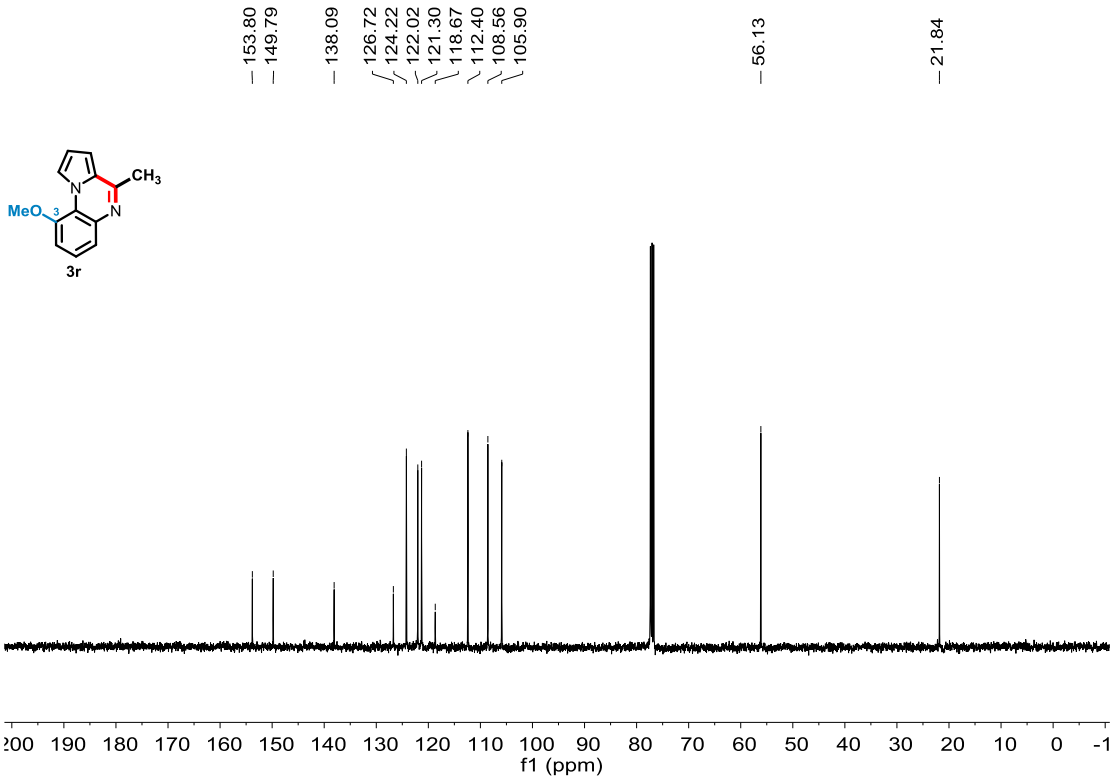

7.97
7.87
7.80
7.80
6.94
6.93
6.90
6.90
6.89
2.72
CH3
N
N
Cl
4
5
Cl
3p
0.88
0.95
0.94
0.94
0.94
3.00
8.0 7.8 7.6 7.4 7.2 7.0 6.8
f1 (ppm)
0.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

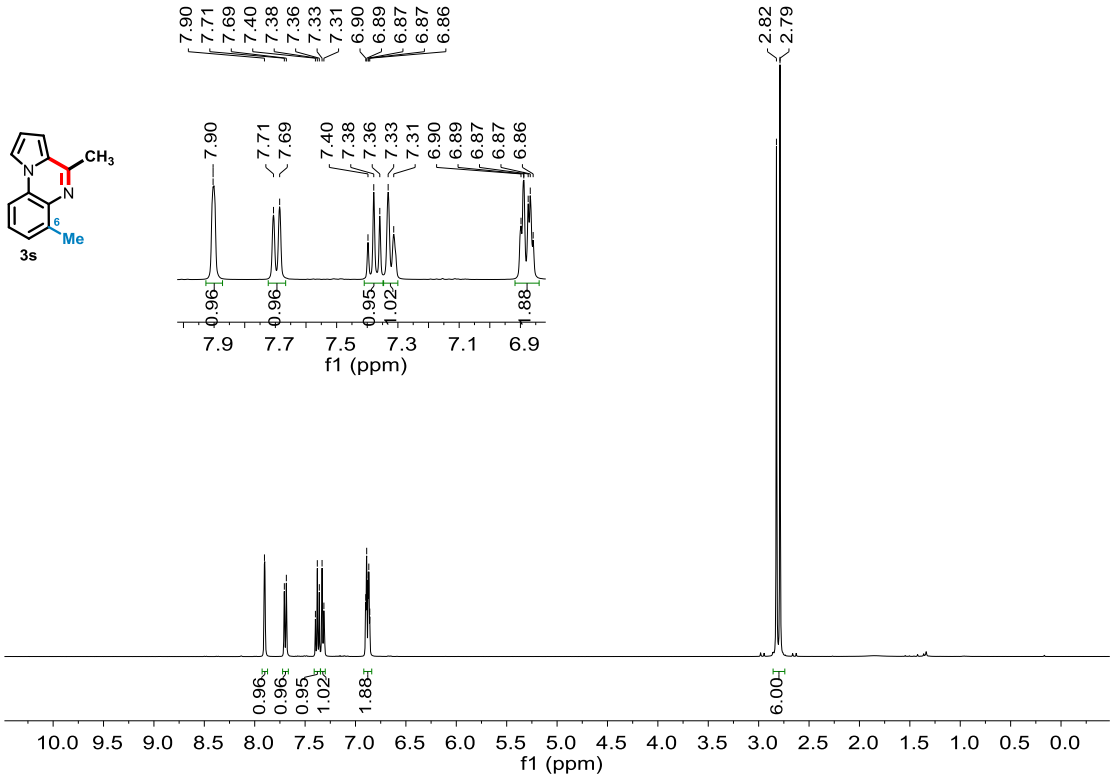

155.04
135.35
130.30
130.21
128.58
126.37
125.98
115.13
114.72
114.29
107.58
21.93
CH3
N
N
Cl
4
Cl
5
3p
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

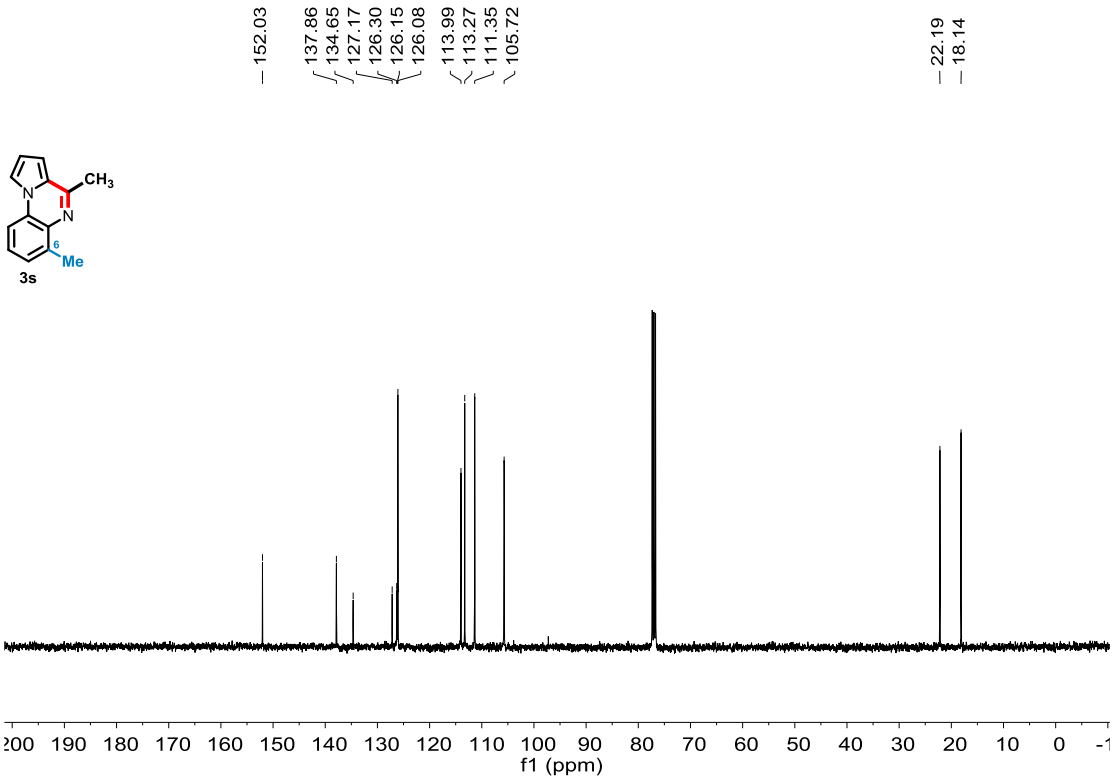

8.36
8.35
7.88
7.86
7.38
7.36
7.35
7.33
7.00
6.99
6.90
6.90
6.89
2.99
2.79
CH3
N
N
Me
3
3q
0.94
0.93
1.70
0.90
0.89
8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8
f1 (ppm)
3.00
2.85
0.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

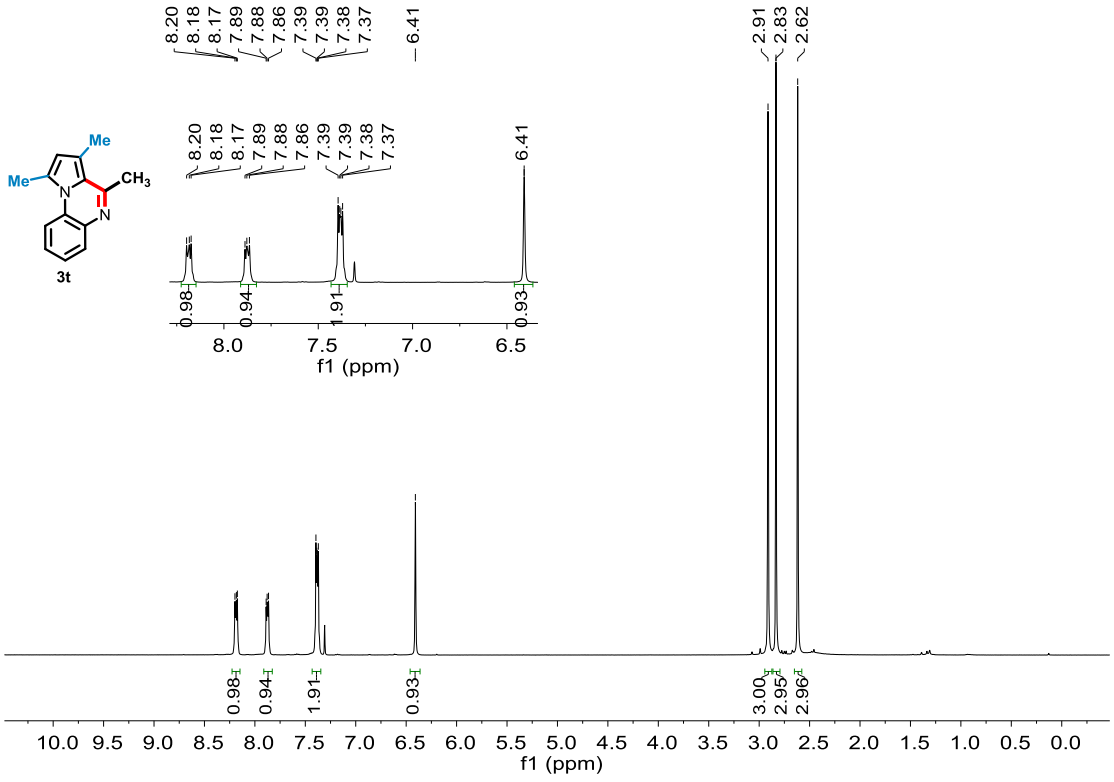

153.13
137.11
130.57
127.57
127.47
125.34
124.63
120.20
112.97
106.40
23.80
21.60
CH3
Me
3
N
N
3q
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

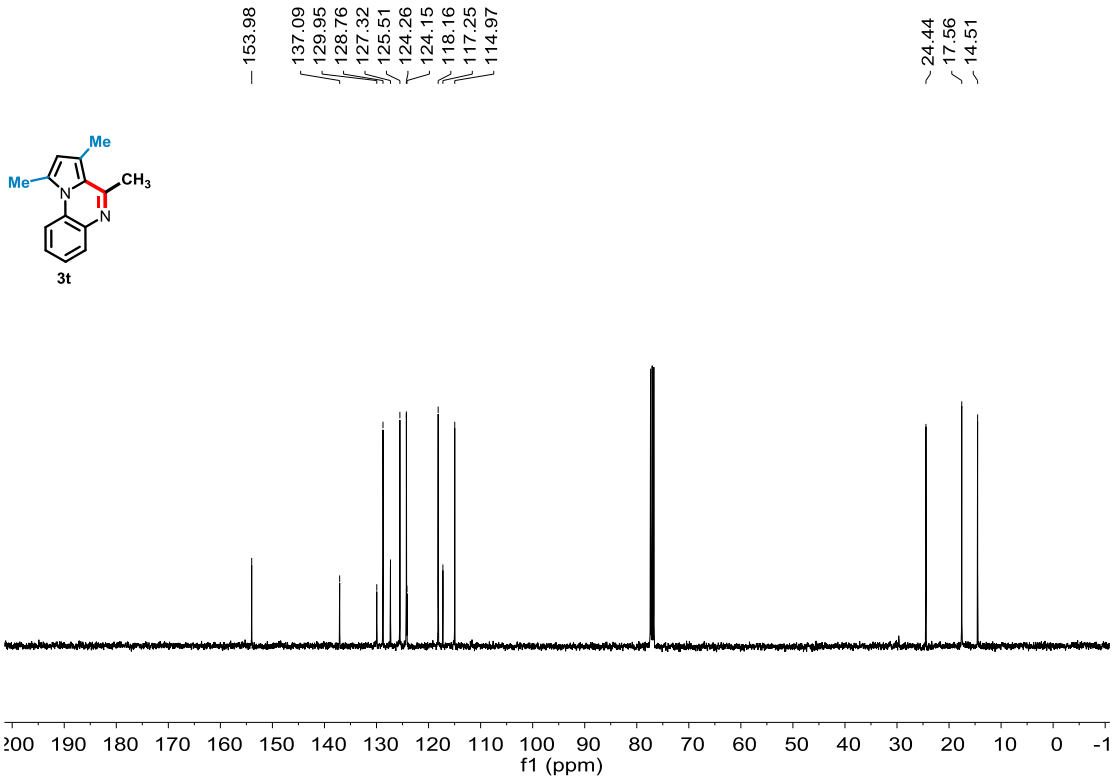

8.75
8.74
7.59
7.57
7.38
7.36
7.34
7.05
7.03
6.95
6.94
6.84
6.83
6.82
4.09
2.76
CH3
MeO
3
N
N
3r
0.92
0.93
0.96
0.97
0.93
0.93
3.00
2.97
8.8 8.4 8.0 7.6 7.2 6.8
f1 (ppm)
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


153.80
149.79
138.09
126.72
124.22
122.02
121.30
118.67
112.40
108.56
105.90
56.13
21.84
MeO
3
CH3
N
N
3r
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


7.90
7.71
7.69
7.40
7.38
7.36
7.33
7.31
6.90
6.89
6.87
6.87
6.86
2.82
2.79
CH3
N
N
6
Me
3s
0.96
0.96
0.95
1.02
1.88
6.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
7.9 7.7 7.5 7.3 7.1 6.9
f1 (ppm)


152.03
137.86
134.65
127.17
126.30
126.15
126.08
113.99
113.27
111.35
105.72
22.19
18.14
CH3
N
N
6
Me
3s
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


8.20
8.18
8.17
7.89
7.88
7.86
7.39
7.39
7.38
7.37
6.41
2.91
2.83
2.62
Me
Me
CH3
N
N
3t
0.98
0.94
1.91
0.93
8.0
7.5
7.0
6.5
f1 (ppm)
0.98
0.94
1.91
0.93
3.00
2.95
2.96
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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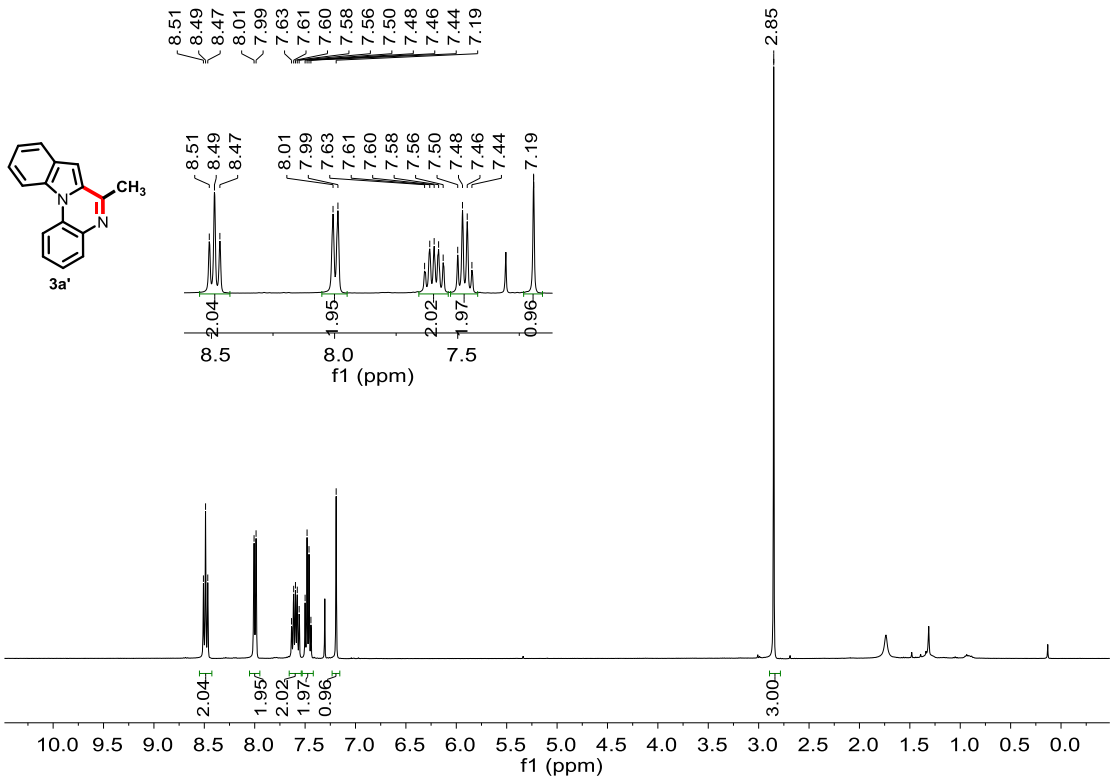
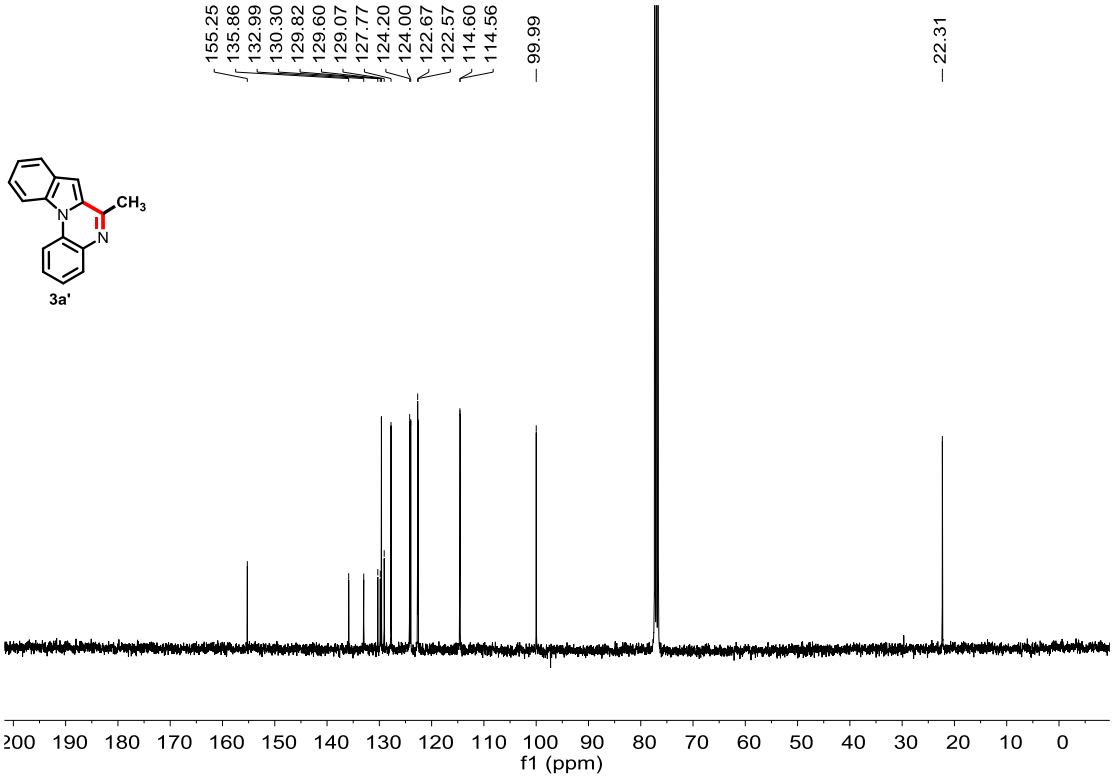
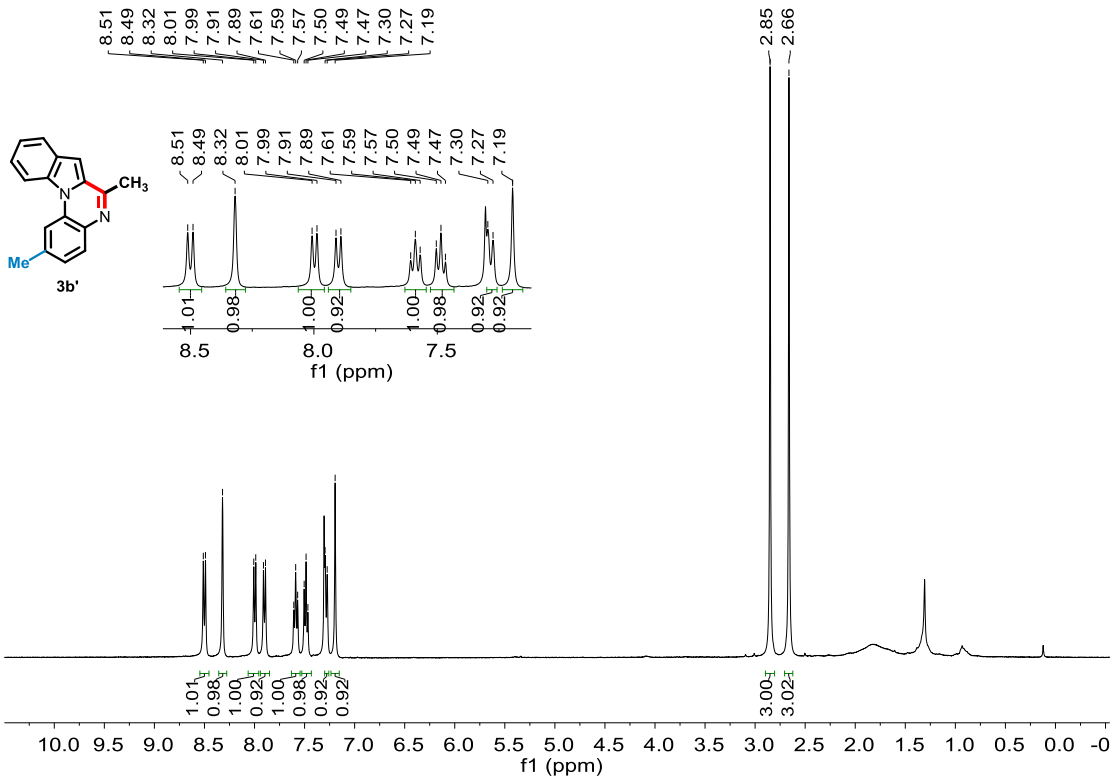
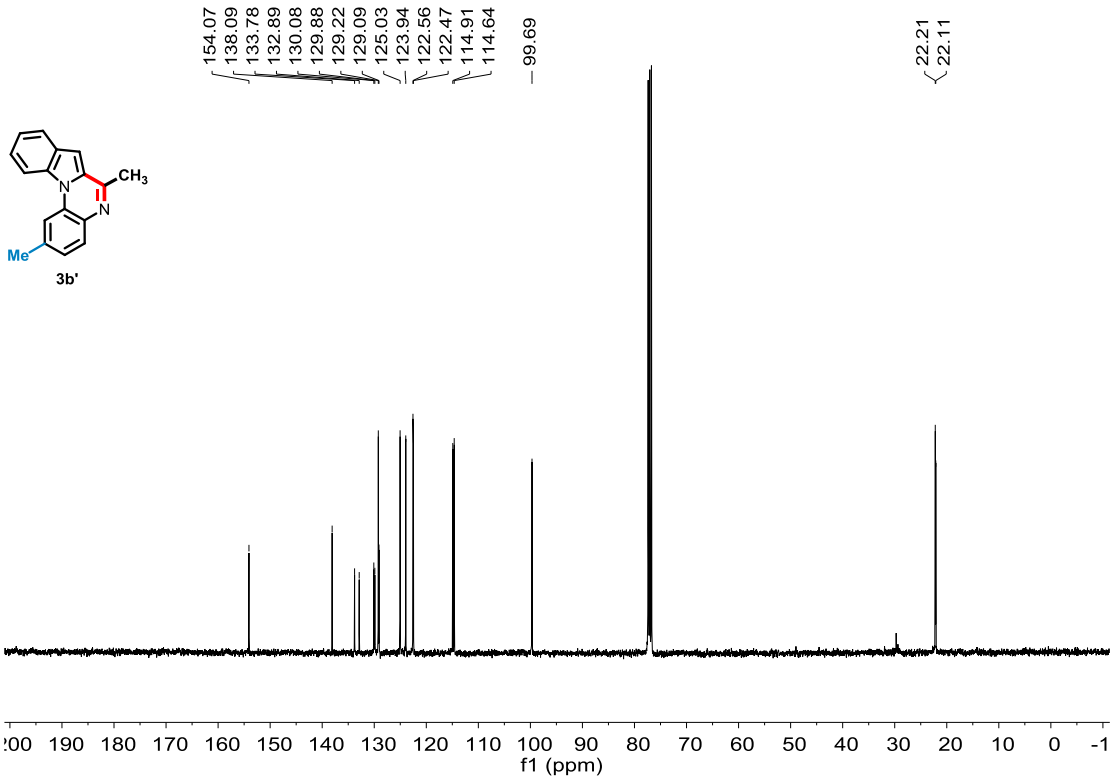
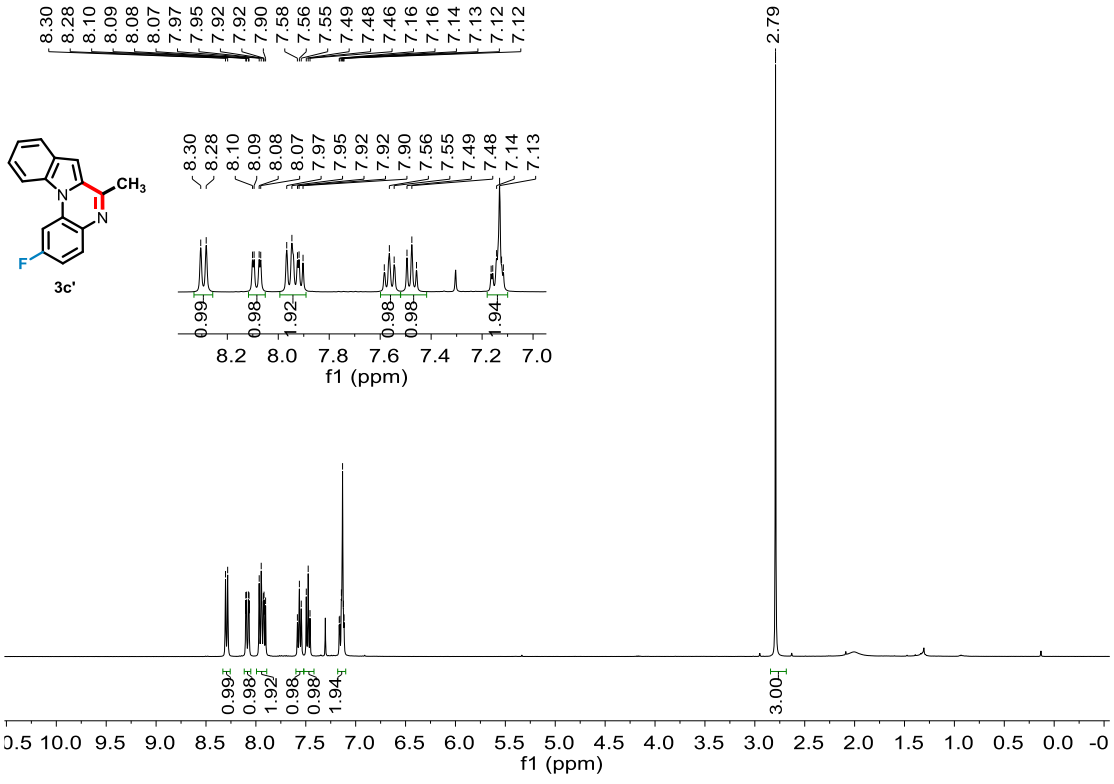
137.09
129.95
128.76
127.32
125.51
124.26
124.15
118.16
117.25
114.97
24.44
17.56
14.51
Me
Me
CH3
N
N
3t
f1 (ppm)

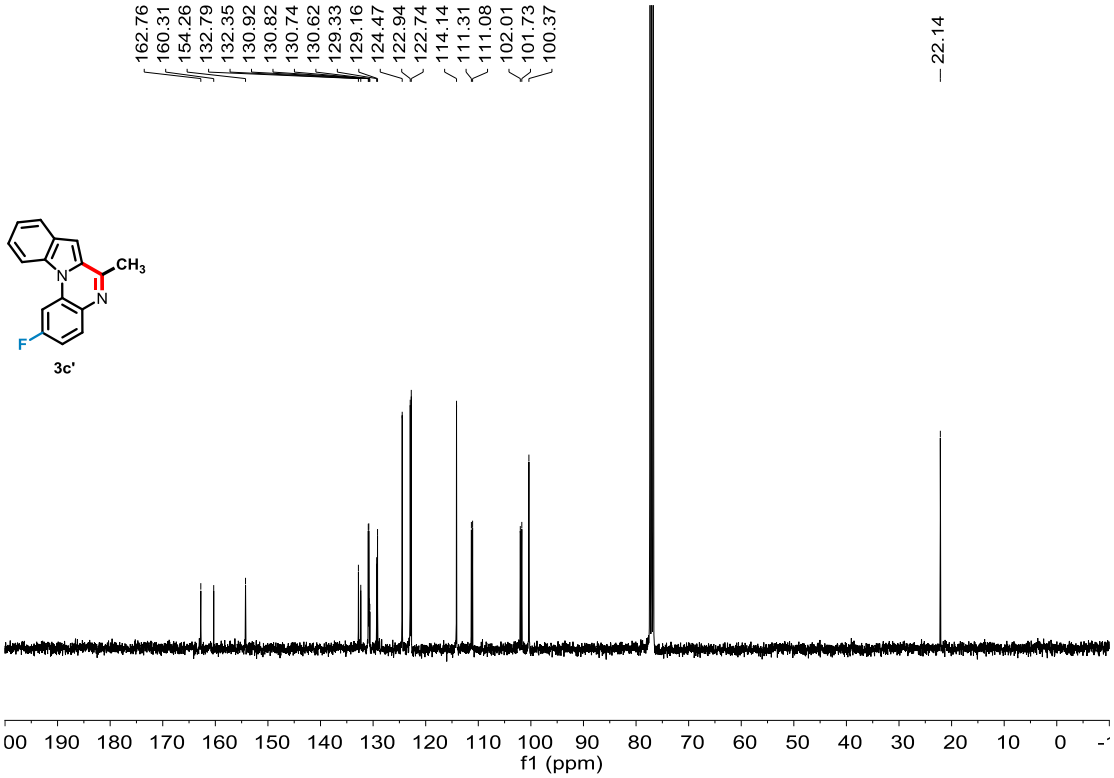

8.51
8.49
8.47
8.01
7.99
7.63
7.61
7.60
7.58
7.56
7.50
7.48
7.46
7.44
7.19
2.85
CH3
N
N
3a'
2.04
1.95
2.02
1.97
0.96
3.00
f1 (ppm)

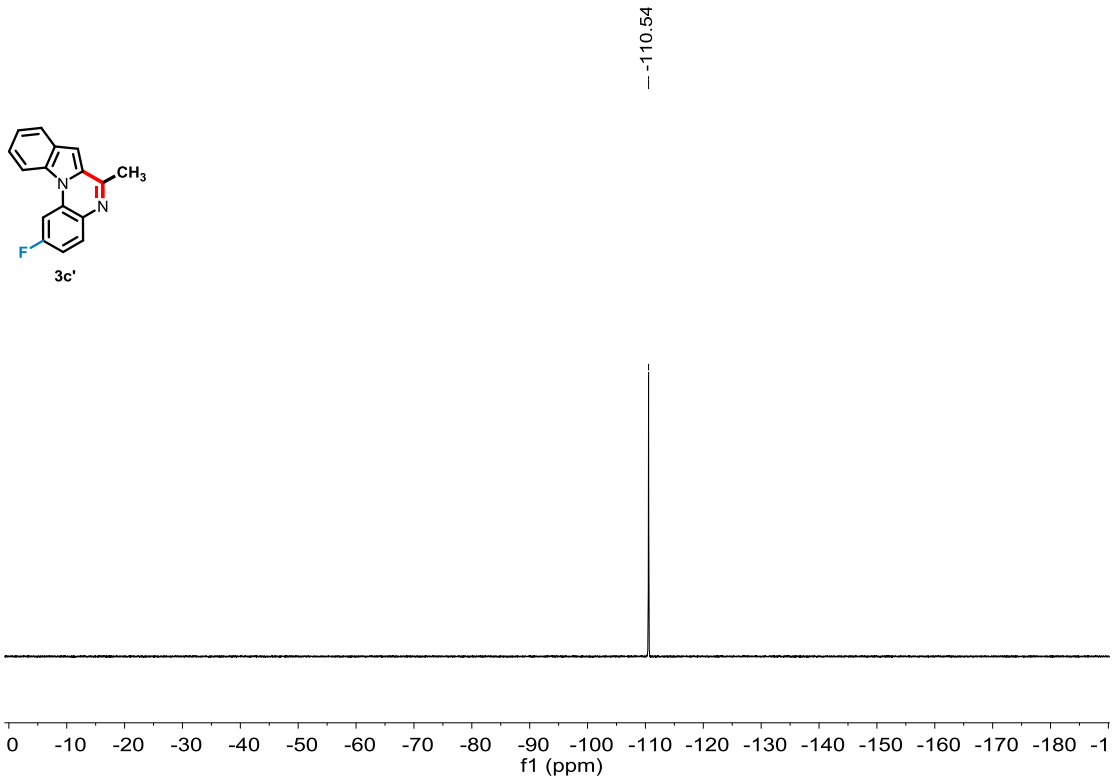

155.25
135.86
132.99
130.30
129.82
129.60
129.07
127.77
124.20
124.00
122.67
122.57
114.60
114.56
99.99
22.31
CH3
N
N
3a'
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

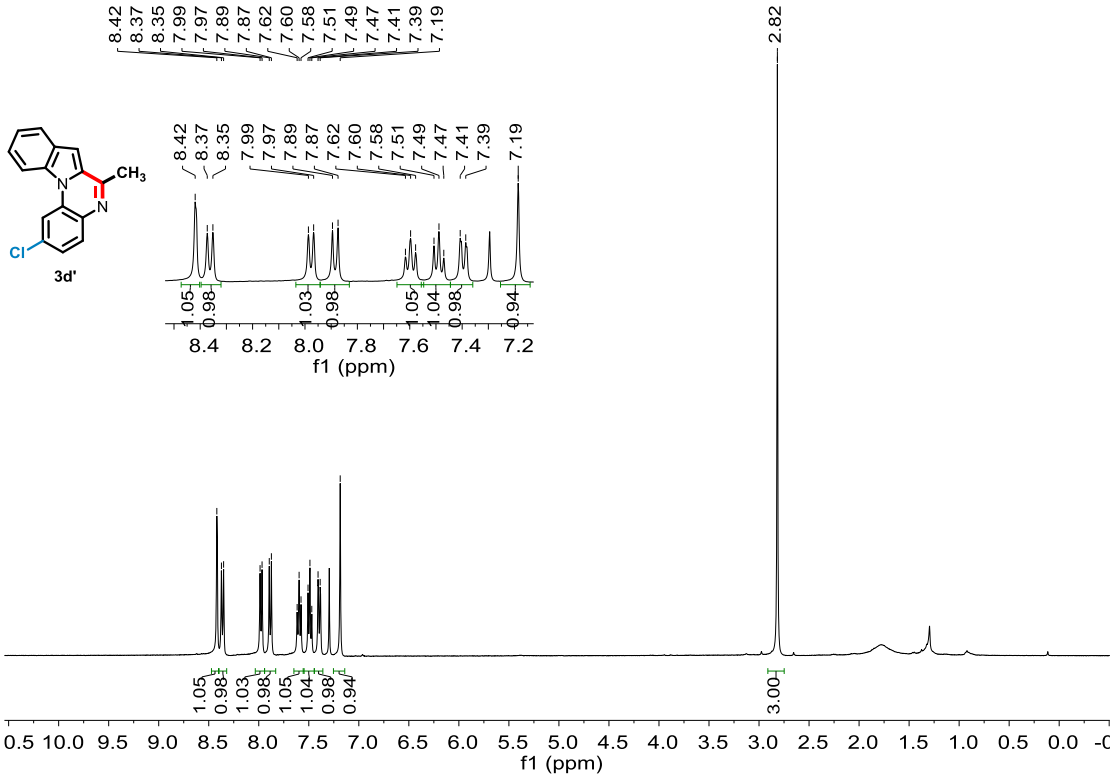

8.51
8.49
8.32
8.01
7.99
7.91
7.89
7.61
7.59
7.57
7.50
7.49
7.47
7.30
7.27
7.19
2.85
2.66
CH3
N
N
Me
3b'
1.01
0.98
1.00
0.92
1.00
0.98
0.92
0.92
3.00
3.02
8.5
8.0
7.5
f1 (ppm)
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

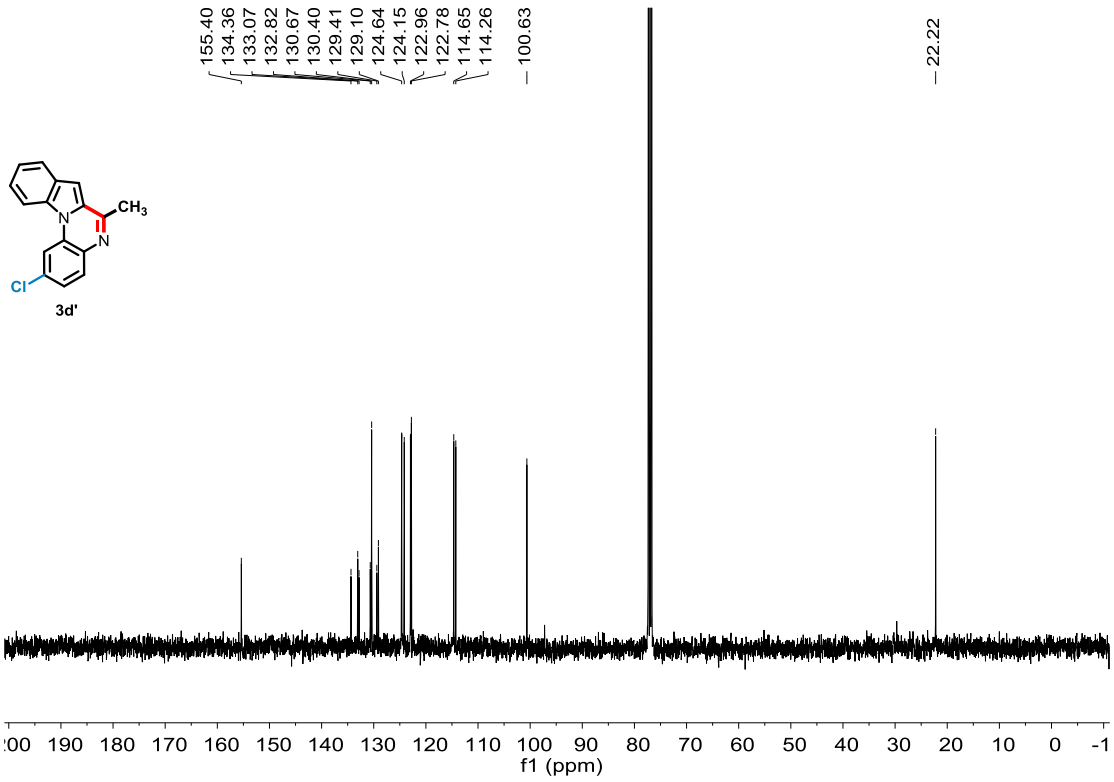

154.07
138.09
133.78
132.89
130.08
129.88
129.22
129.09
125.03
123.94
122.56
122.47
114.91
114.64
99.69
22.21
22.11
CH3
N
N
Me
3b'
f1 (ppm)

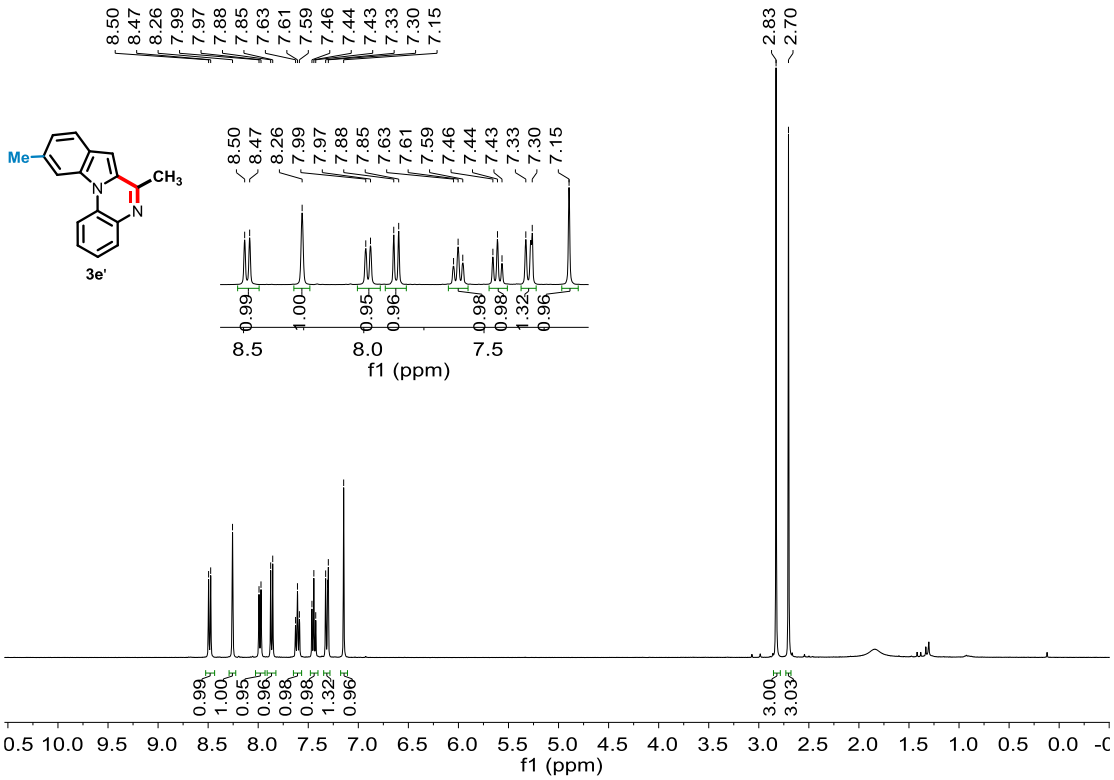

8.30
8.28
8.10
8.09
8.08
8.07
7.97
7.95
7.92
7.92
7.90
7.58
7.56
7.55
7.49
7.48
7.46
7.16
7.16
7.14
7.13
7.12
2.79
CH3
N
N
F
3c'
0.99
0.98
1.92
0.98
0.98
1.94
3.00
f1 (ppm)

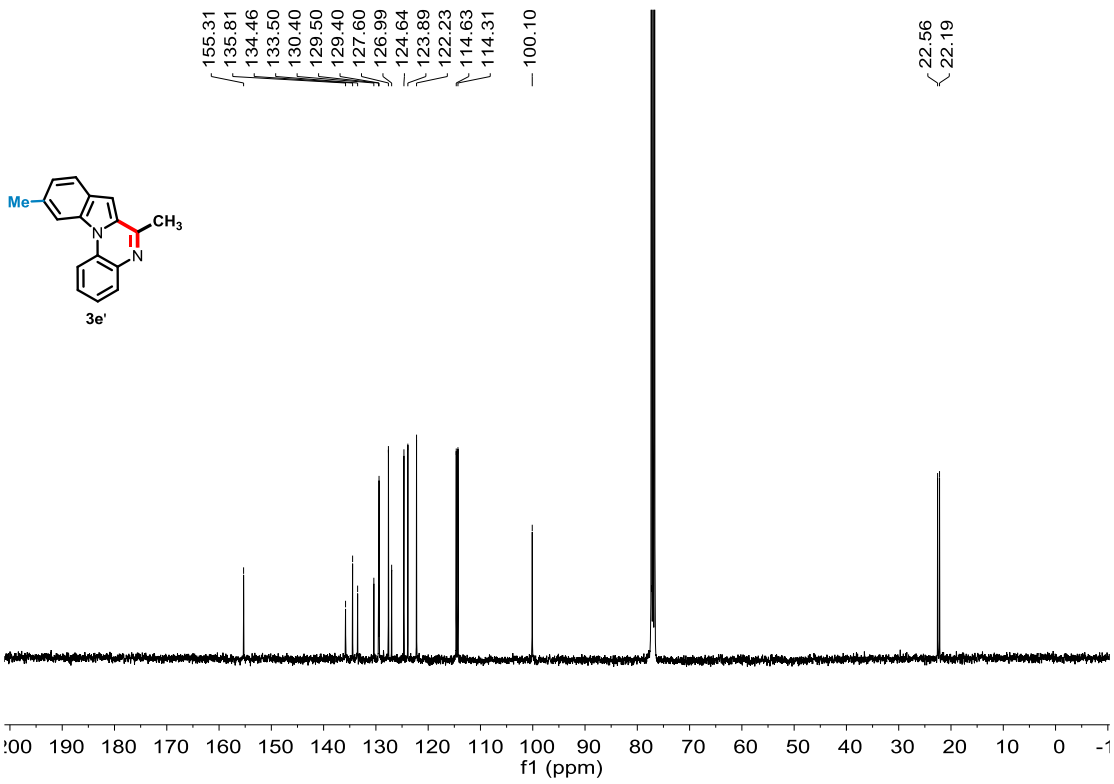

162.76
160.31
154.26
132.79
132.35
130.92
130.82
130.74
130.62
129.33
129.16
124.47
122.94
122.74
114.14
111.31
111.08
102.01
101.73
100.37
22.14
CH3
N
N
F
3c'
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

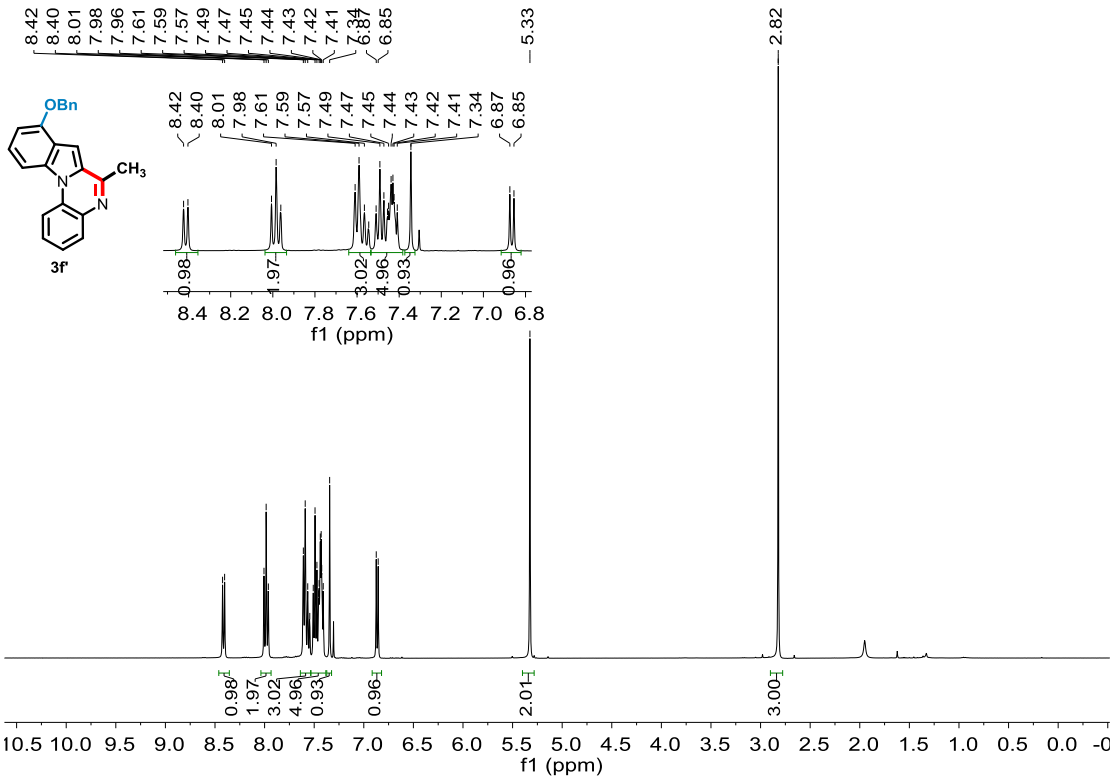

-110.54
CH3
N
N
F
3c'
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -1
f1 (ppm)

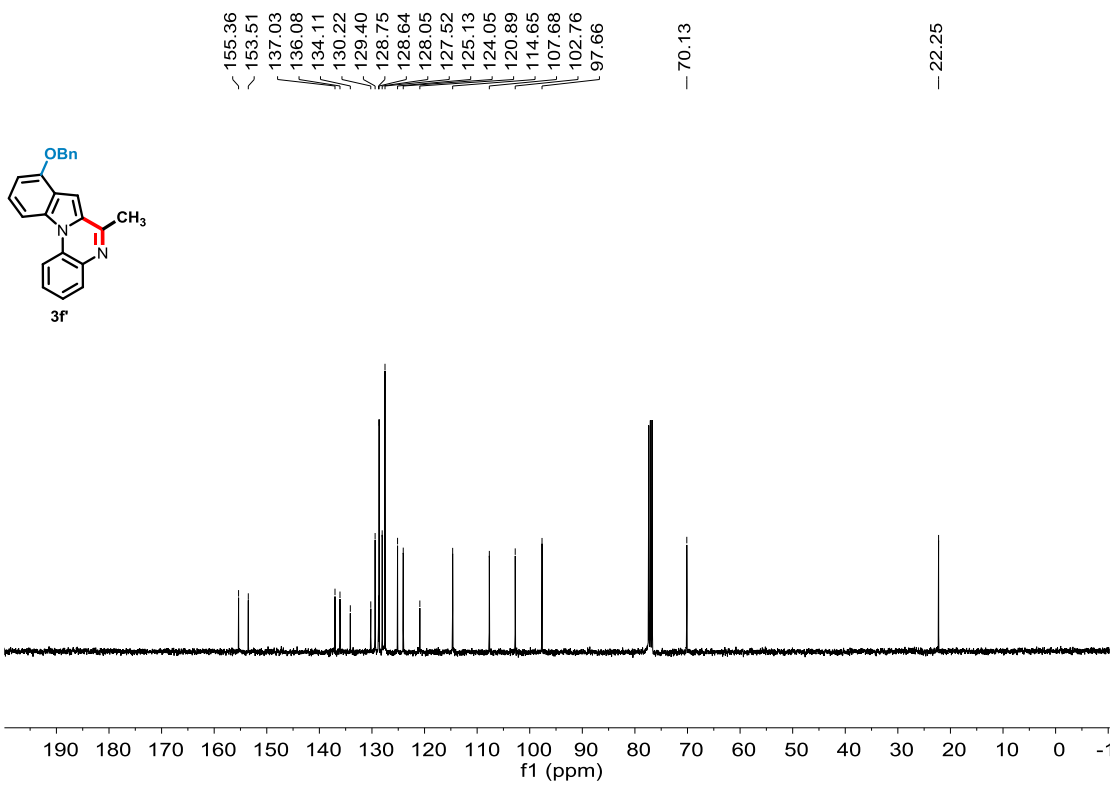

8.42
8.37
8.35
7.99
7.97
7.89
7.87
7.62
7.60
7.58
7.51
7.49
7.47
7.41
7.39
7.19
2.82
CH3
N
N
Cl
3d'
1.05
0.98
1.03
0.98
1.05
1.04
0.98
0.94
3.00
f1 (ppm)

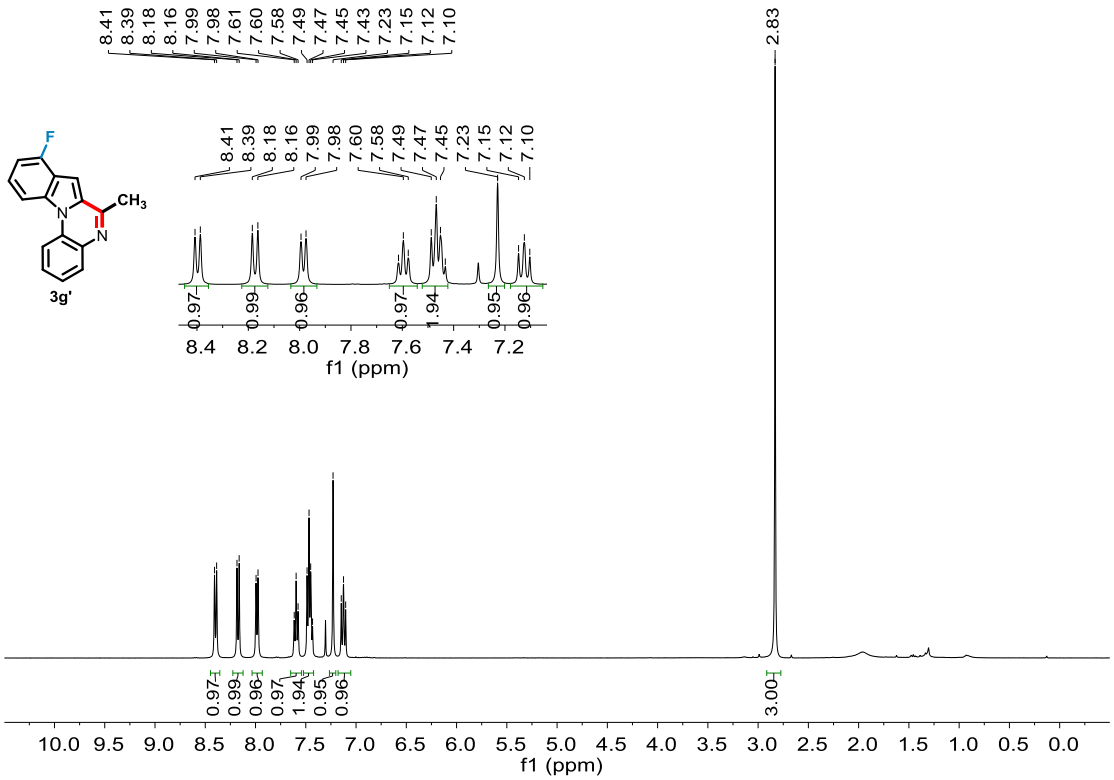

155.40
134.36
133.07
132.82
130.67
130.40
129.41
129.10
124.64
124.15
122.96
122.78
114.65
114.26
100.63
22.22
CH3
N
N
Cl
3d'
f1 (ppm)

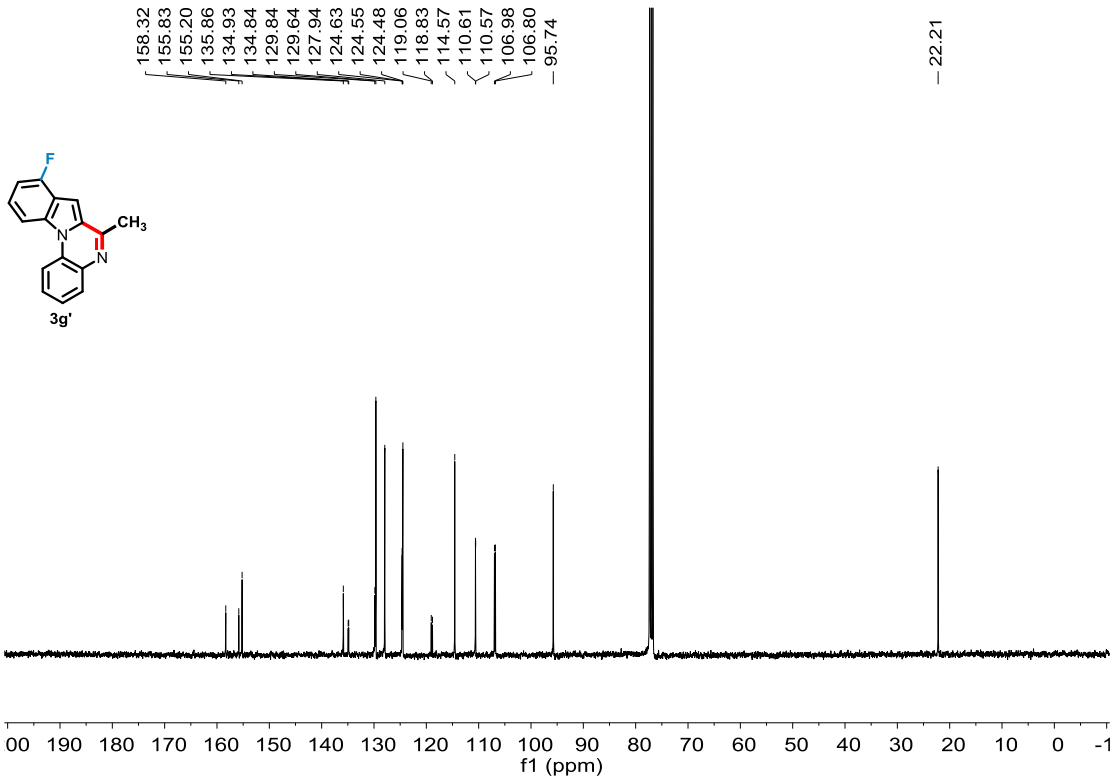

8.50
8.47
8.26
7.99
7.97
7.88
7.85
7.63
7.61
7.59
7.46
7.44
7.43
7.33
7.30
7.15
2.83
2.70
Me
CH3
N
N
3e'
0.99
1.00
0.95
0.96
0.98
1.32
0.96
3.00
3.03
8.5
8.0
7.5
f1 (ppm)
0.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

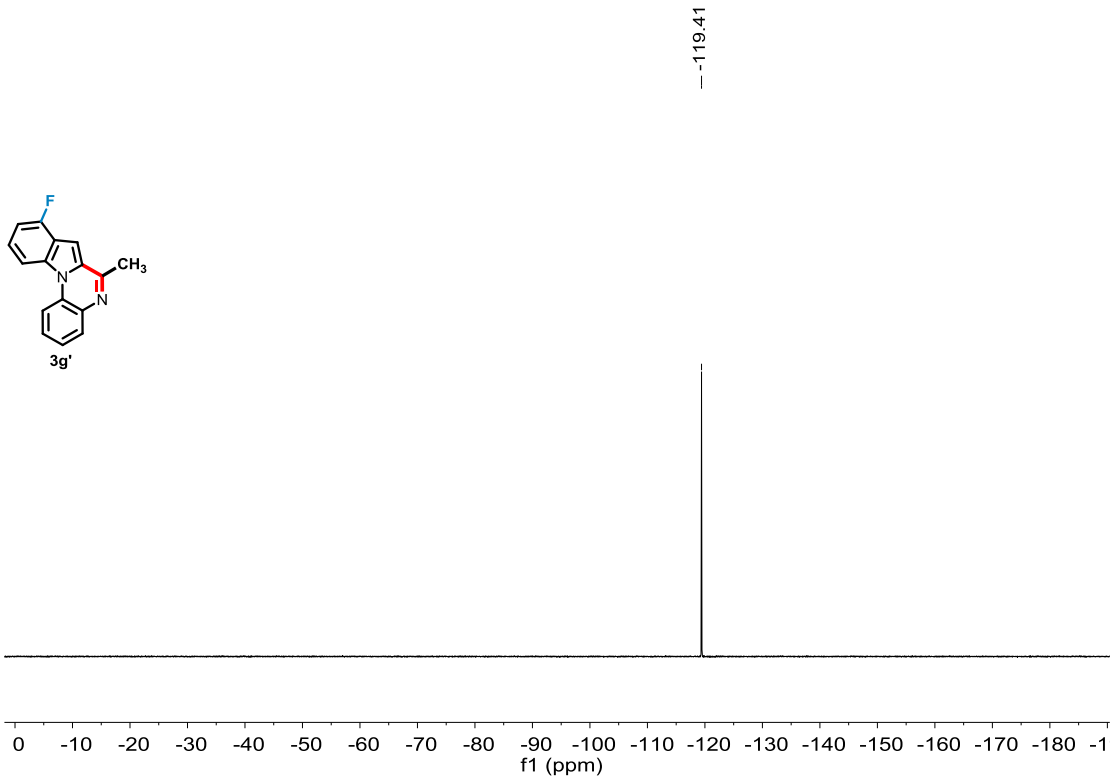

155.31
135.81
134.46
133.50
130.40
129.50
129.40
127.60
126.99
124.64
123.89
122.23
114.63
114.31
100.10
22.56
22.19
Me
CH3
N
N
3e'
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

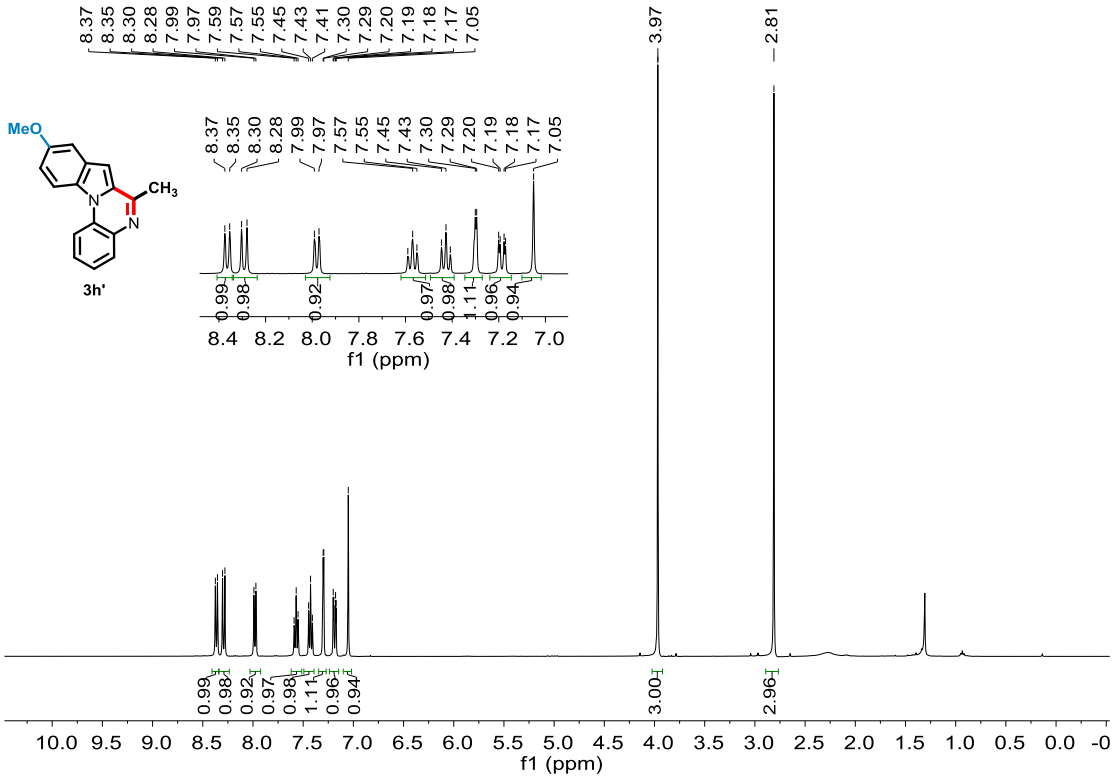

8.42
8.40
8.01
7.98
7.96
7.61
7.59
7.57
7.49
7.47
7.45
7.44
7.43
7.42
7.41
7.34
6.87
6.85
5.33
2.82
OBn
CH3
N
N
3f'
0.98
1.97
3.02
4.96
0.93
0.96
8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8
f1 (ppm)
0.98
1.97
3.02
4.96
0.93
0.96
2.01
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

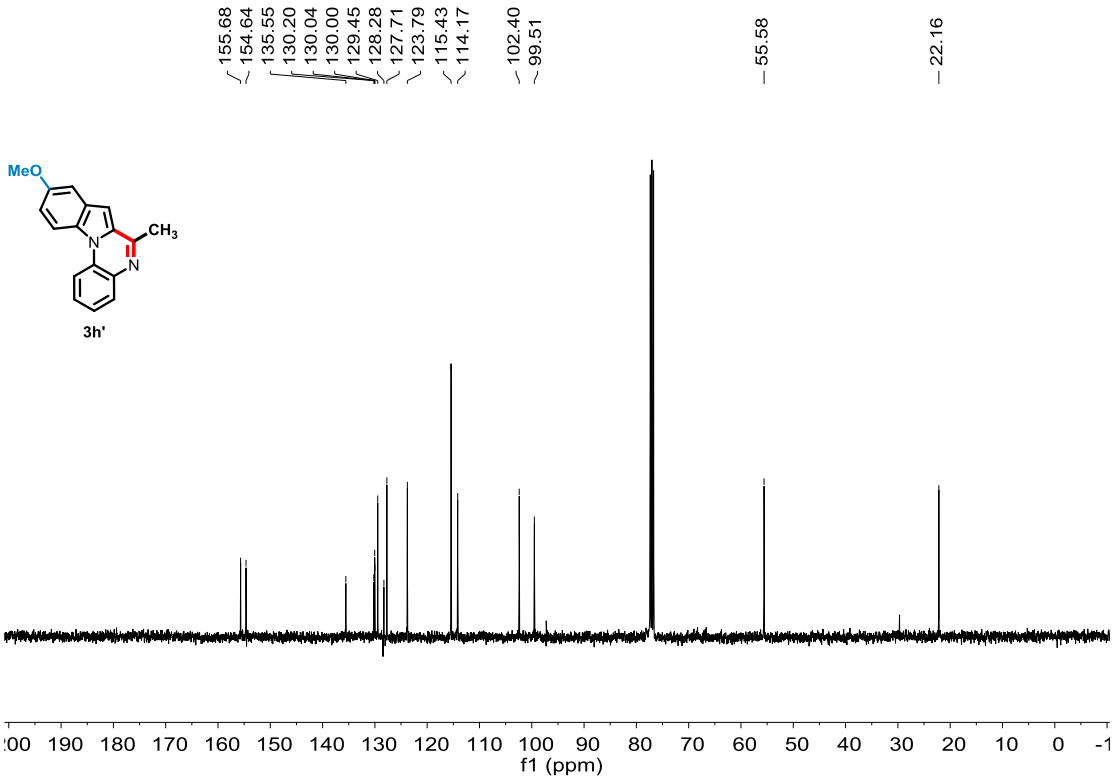

155.36
153.51
137.03
136.08
134.11
130.22
129.40
128.75
128.64
128.05
127.52
125.13
124.05
120.89
114.65
107.68
102.76
97.66
70.13
22.25
OBn
CH3
N
N
3f'
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

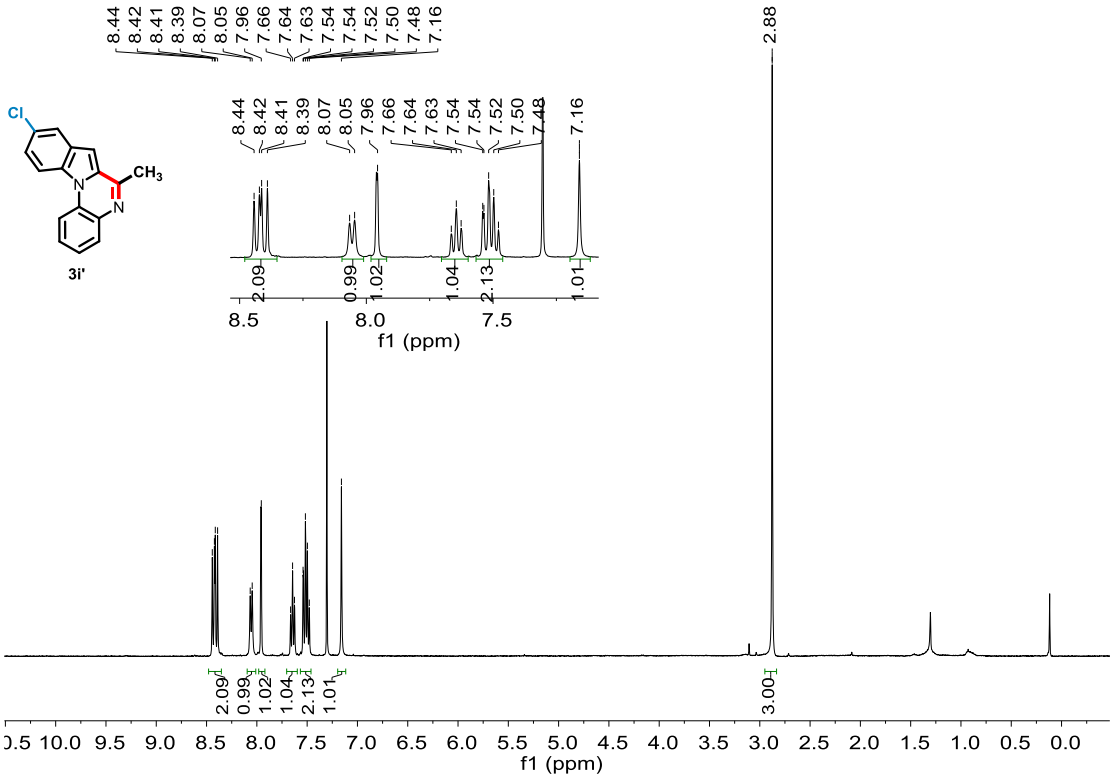

8.41
8.39
8.18
8.16
7.99
7.98
7.61
7.60
7.58
7.49
7.47
7.45
7.43
7.23
7.15
7.12
7.10
2.83
F
CH3
N
N
3g'
0.97
0.99
0.96
0.97
1.94
0.95
0.96
3.00
8.4 8.2 8.0 7.8 7.6 7.4 7.2
f1 (ppm)
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

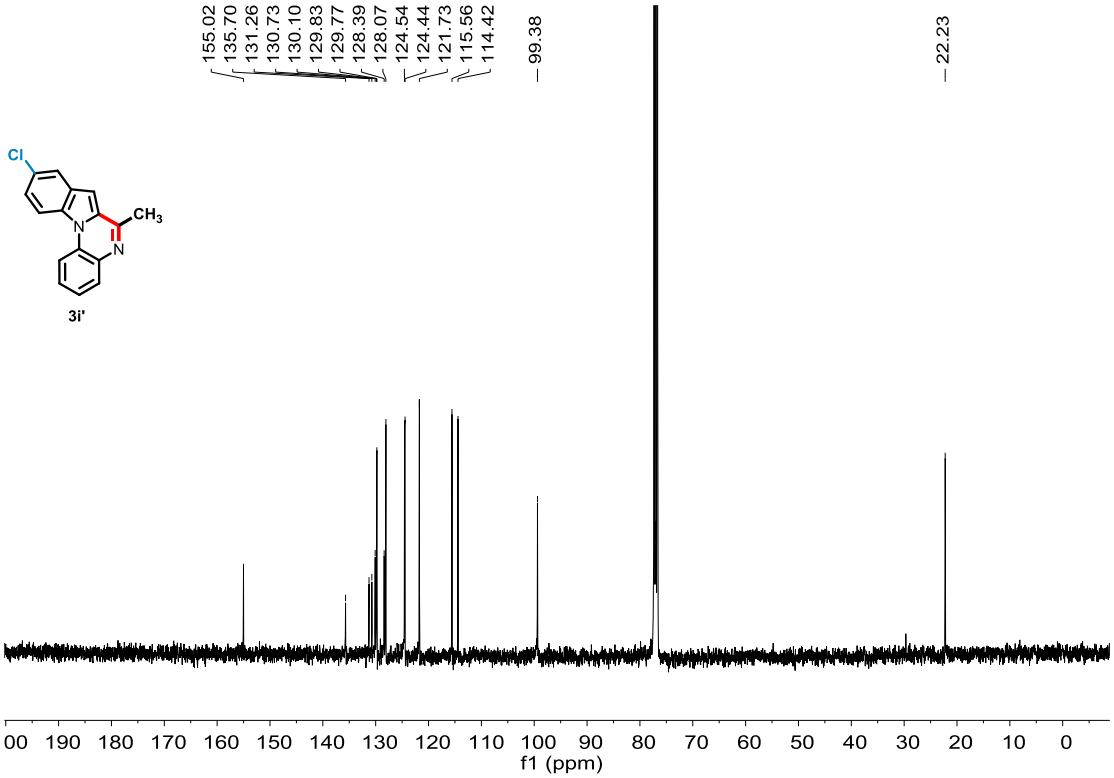

158.32
155.83
155.20
135.86
134.93
134.84
129.84
129.64
127.94
124.63
124.55
124.48
119.06
118.83
114.57
110.61
110.57
106.98
106.80
95.74
22.21
F
CH3
N
N
3g'
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

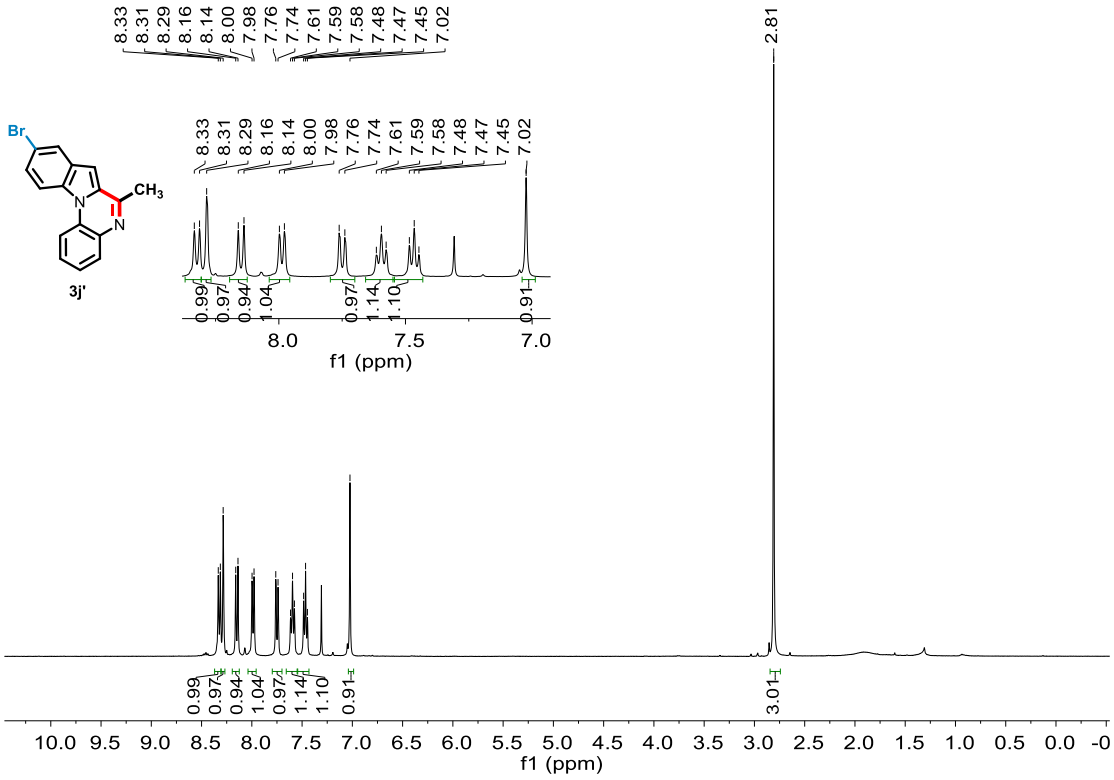

-119.41
F
CH3
N
N
3g'
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -1
f1 (ppm)

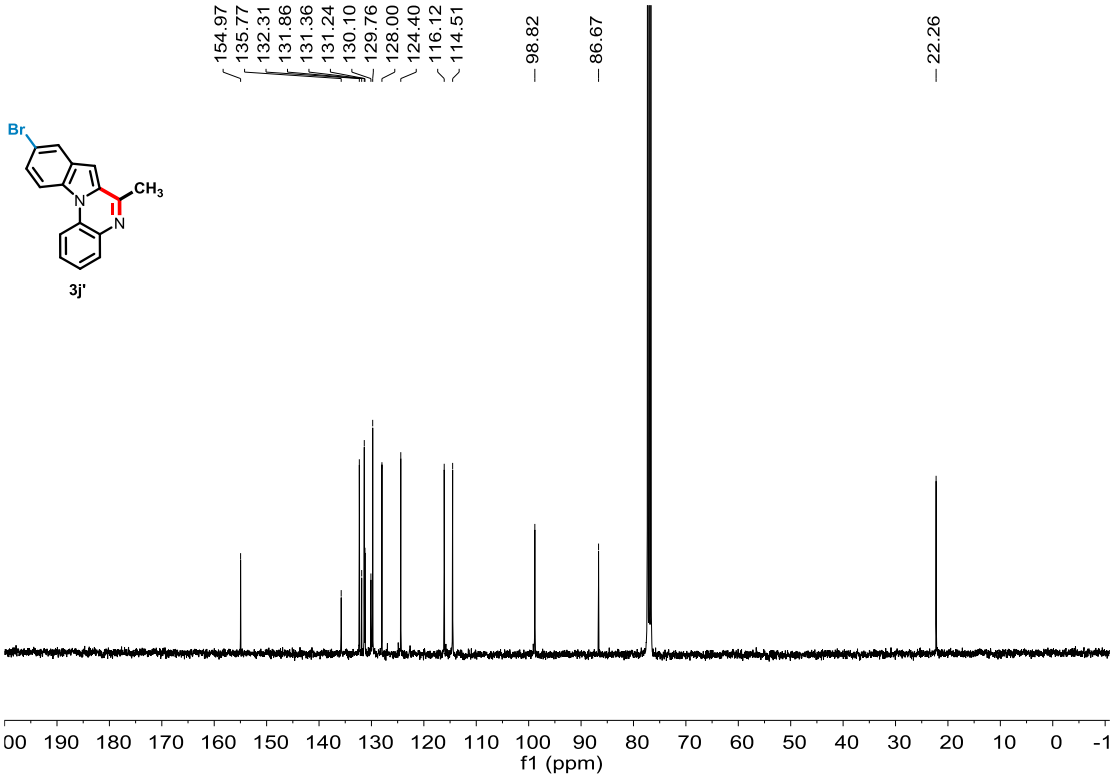

8.37 8.35 8.30 8.28 7.99 7.97 7.59 7.57 7.55 7.45 7.43 7.41 7.30 7.29 7.20 7.19 7.18 7.17 7.05
3.97
2.81
MeO
CH3
N
N
3h'
0.99 0.98 0.92 0.97 0.98 1.11 0.96 0.94
3.00
2.96
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)
8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0
f1 (ppm)

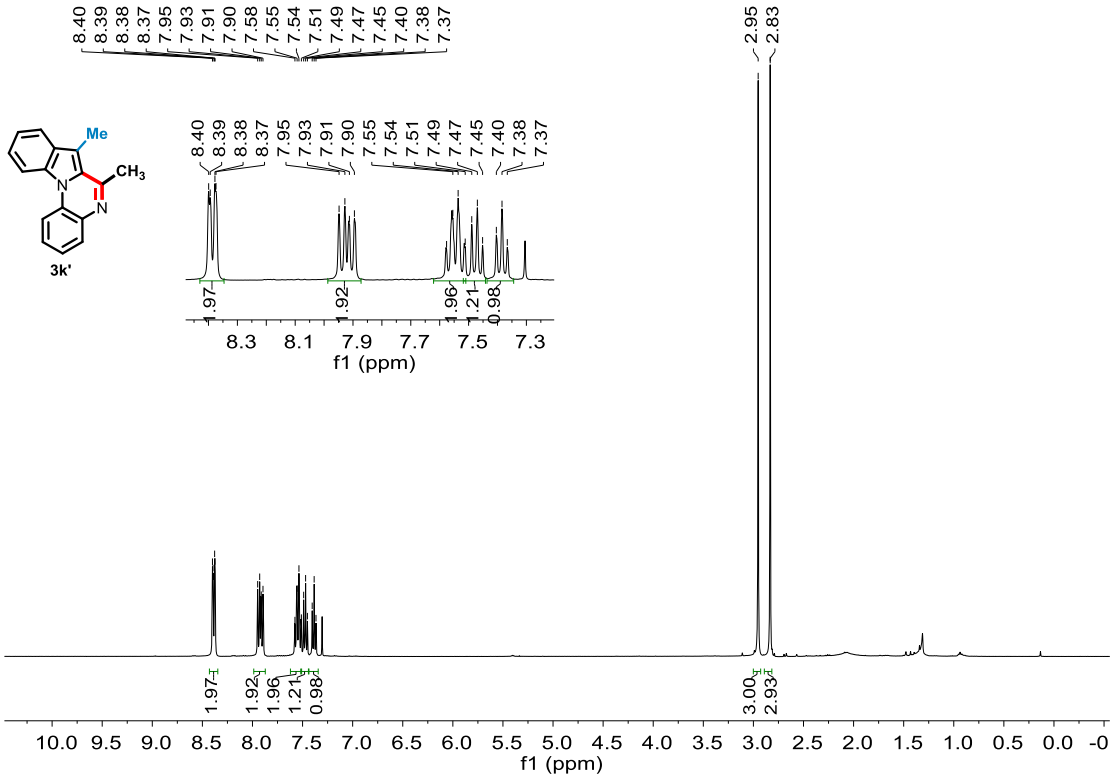

155.68
154.64
135.55
130.20
130.04
130.00
129.45
128.28
127.71
123.79
115.43
114.17
102.40
99.51
55.58
22.16
MeO
CH3
N
N
3h'
f1 (ppm)

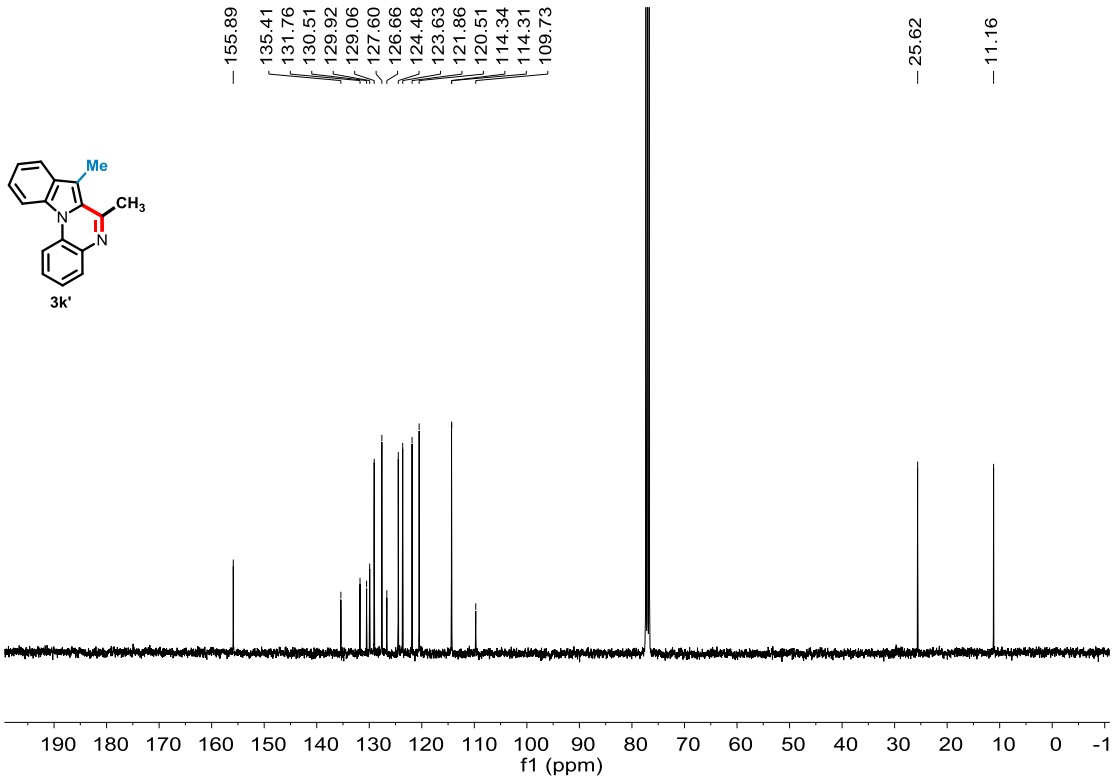

8.44
8.42
8.41
8.39
8.07
8.05
7.96
7.66
7.64
7.63
7.54
7.54
7.52
7.50
7.48
7.16
2.88
Cl
CH3
N
N
3i'
2.09
0.99
1.02
1.04
2.13
1.01
3.00
f1 (ppm)

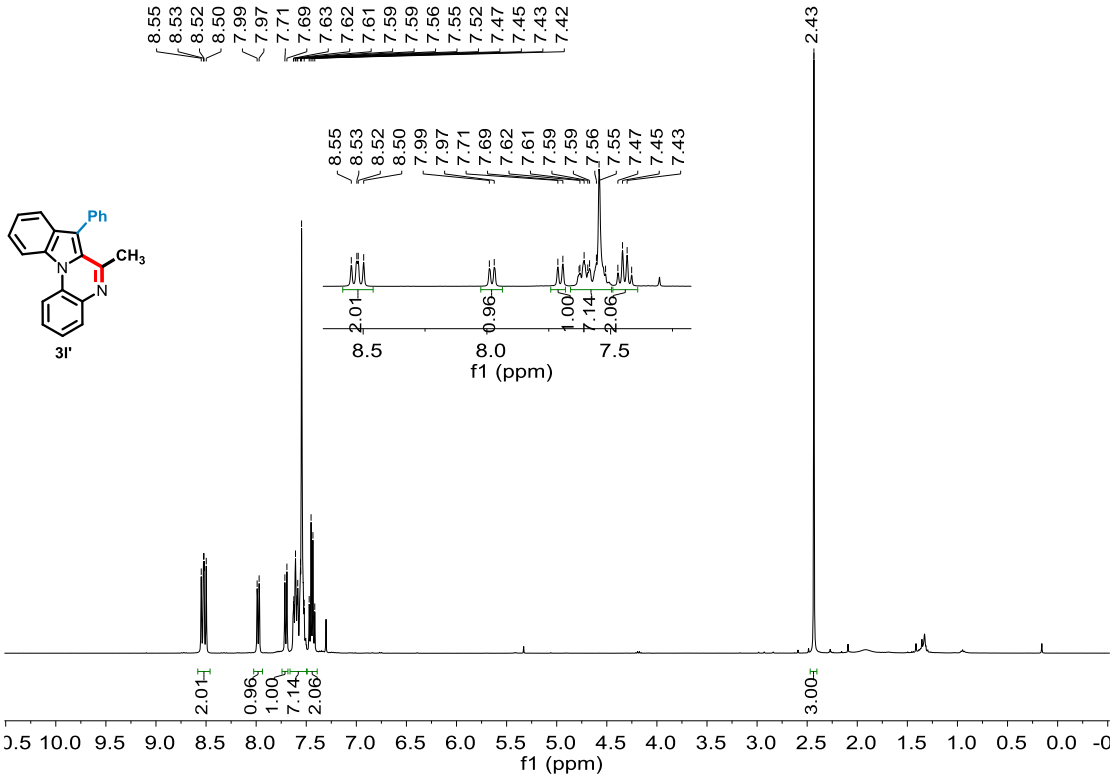

155.02
135.70
131.26
130.73
130.10
129.83
129.77
128.39
128.07
124.54
124.44
121.73
115.56
114.42
99.38
22.23
Cl
CH3
N
N
3i'
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

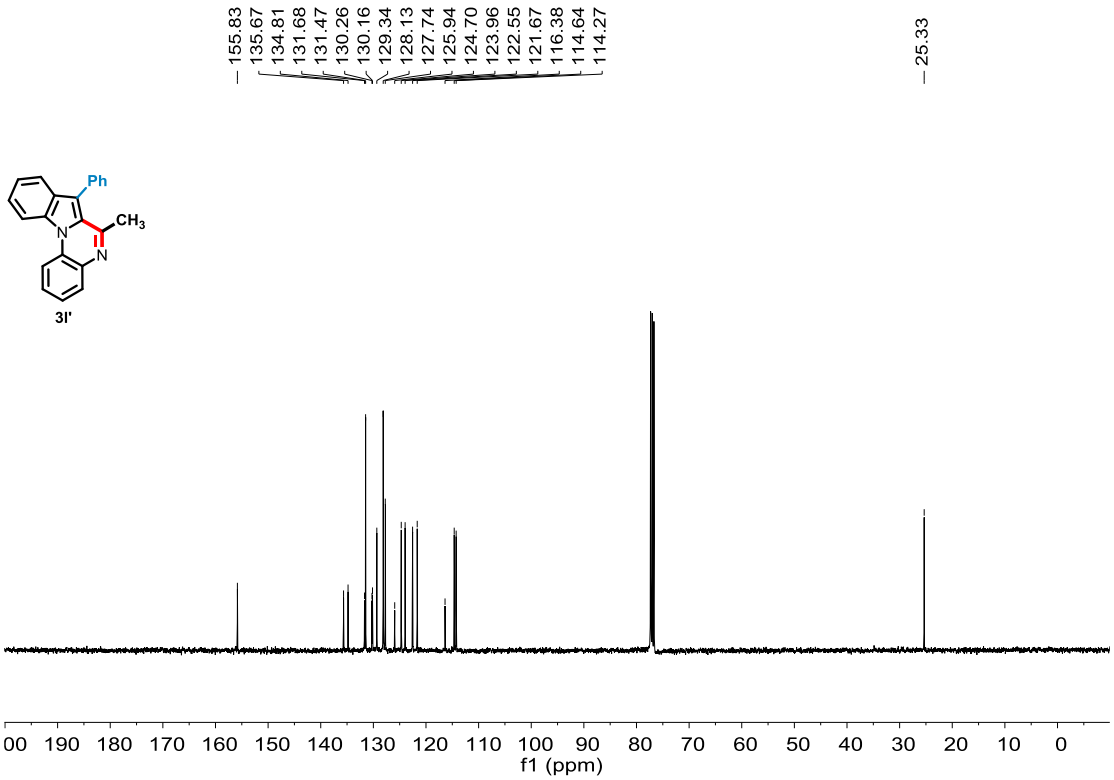

8.33
8.31
8.29
8.16
8.14
8.00
7.98
7.76
7.74
7.61
7.59
7.58
7.48
7.47
7.45
7.02
2.81
Br
CH3
N
N
3j'
0.99
0.97
0.94
1.04
0.97
1.14
1.10
0.91
3.01
8.0
7.5
7.0
f1 (ppm)
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

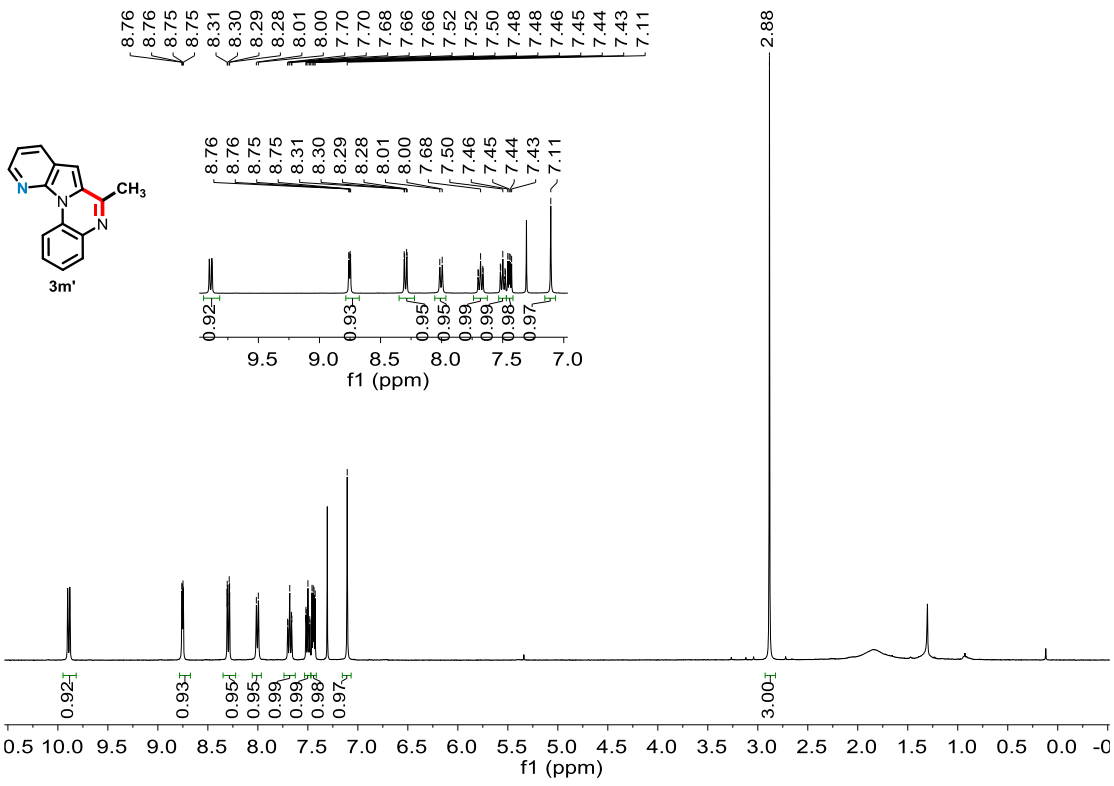

154.97
135.77
132.31
131.86
131.36
131.24
130.10
129.76
128.00
124.40
116.12
114.51
98.82
86.67
22.26
Br
CH3
N
N
3j'
f1 (ppm)

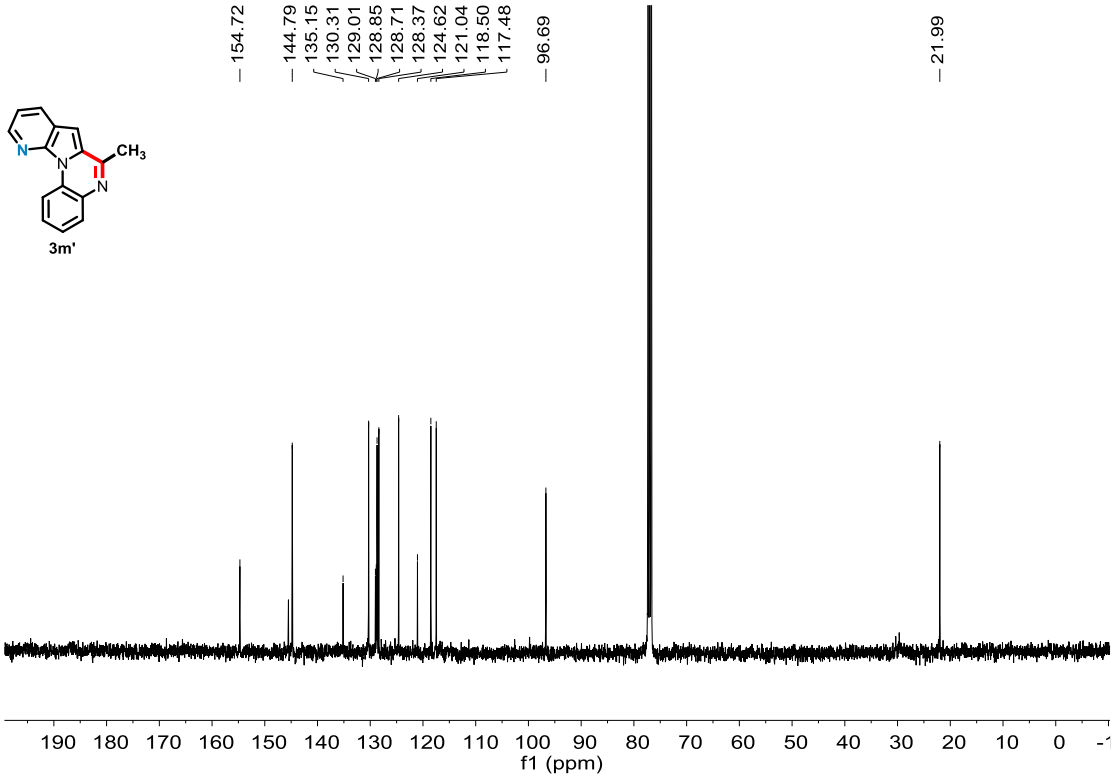

8.40
8.39
8.38
8.37
7.95
7.93
7.91
7.90
7.58
7.55
7.54
7.51
7.49
7.47
7.45
7.40
7.38
7.37
2.95
2.83
Me
CH3
N
N
3k'
1.97
1.92
1.96
1.21
0.98
3.00
2.93
f1 (ppm)

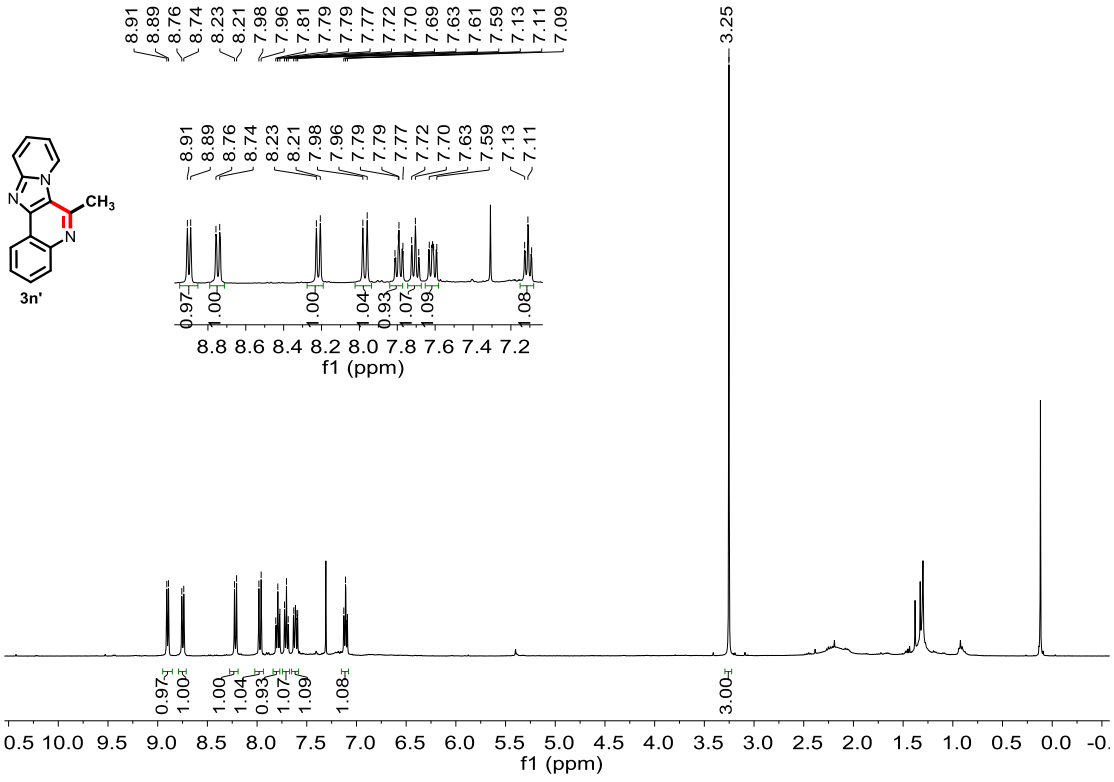

155.89
135.41
131.76
130.51
129.92
129.06
127.60
126.66
124.48
123.63
121.86
120.51
114.34
114.31
109.73
25.62
11.16
Me
CH3
N
N
3k'
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

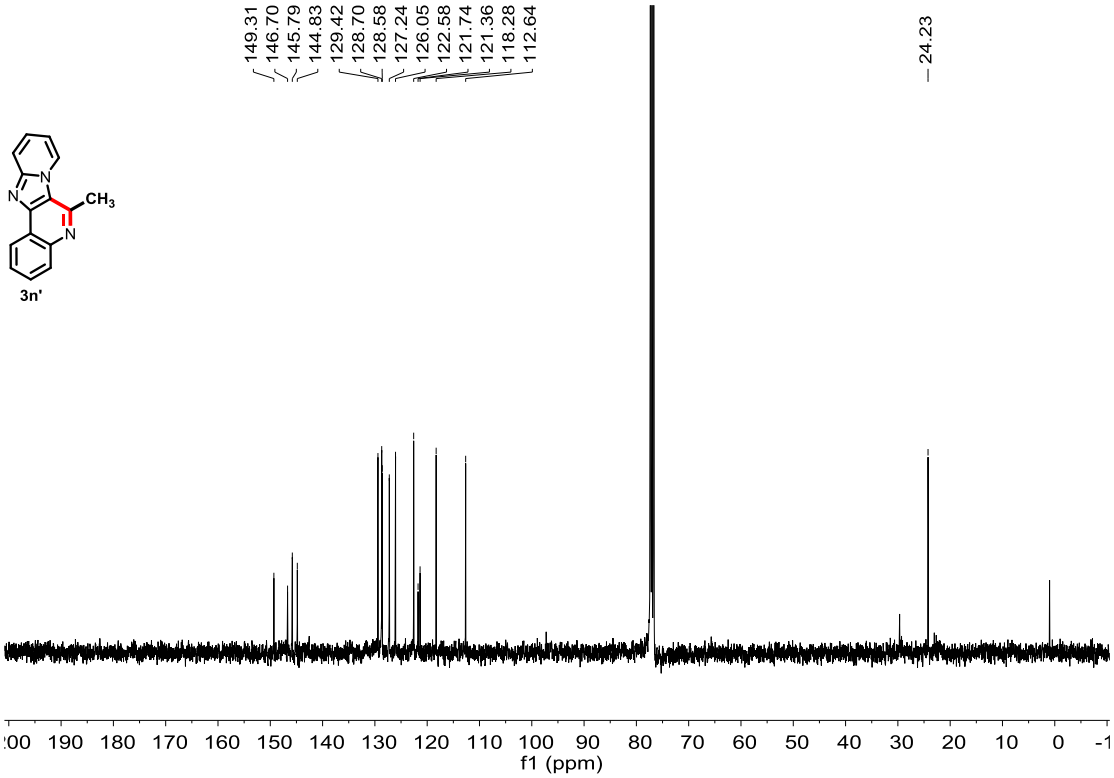

8.55
8.53
8.52
8.50
7.99
7.97
7.71
7.69
7.63
7.62
7.61
7.59
7.59
7.56
7.55
7.52
7.47
7.45
7.43
7.42
2.43
Ph
CH3
N
N
3l'
2.01
0.96
1.00
7.14
2.06
8.5
8.0
7.5
f1 (ppm)
3.00
f1 (ppm)

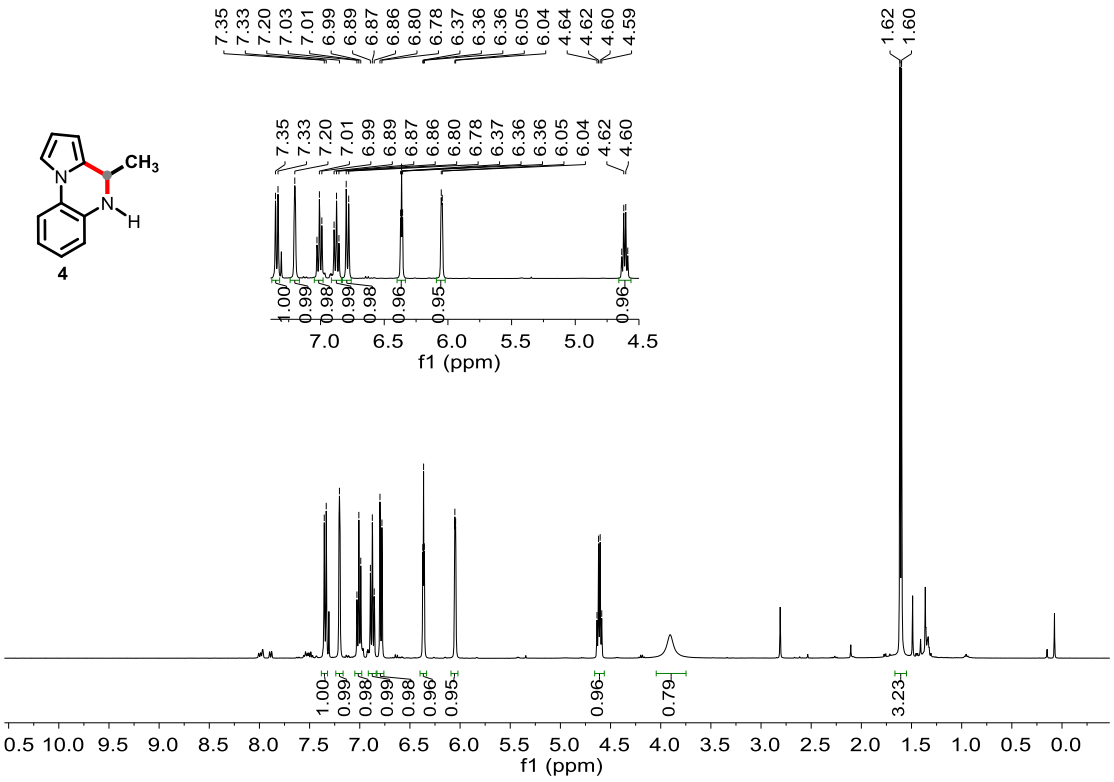

155.83
135.67
134.81
131.68
131.47
130.26
130.16
129.34
128.13
127.74
125.94
124.70
123.96
122.55
121.67
116.38
114.64
114.27
25.33
Ph
CH3
N
N
3l'
f1 (ppm)

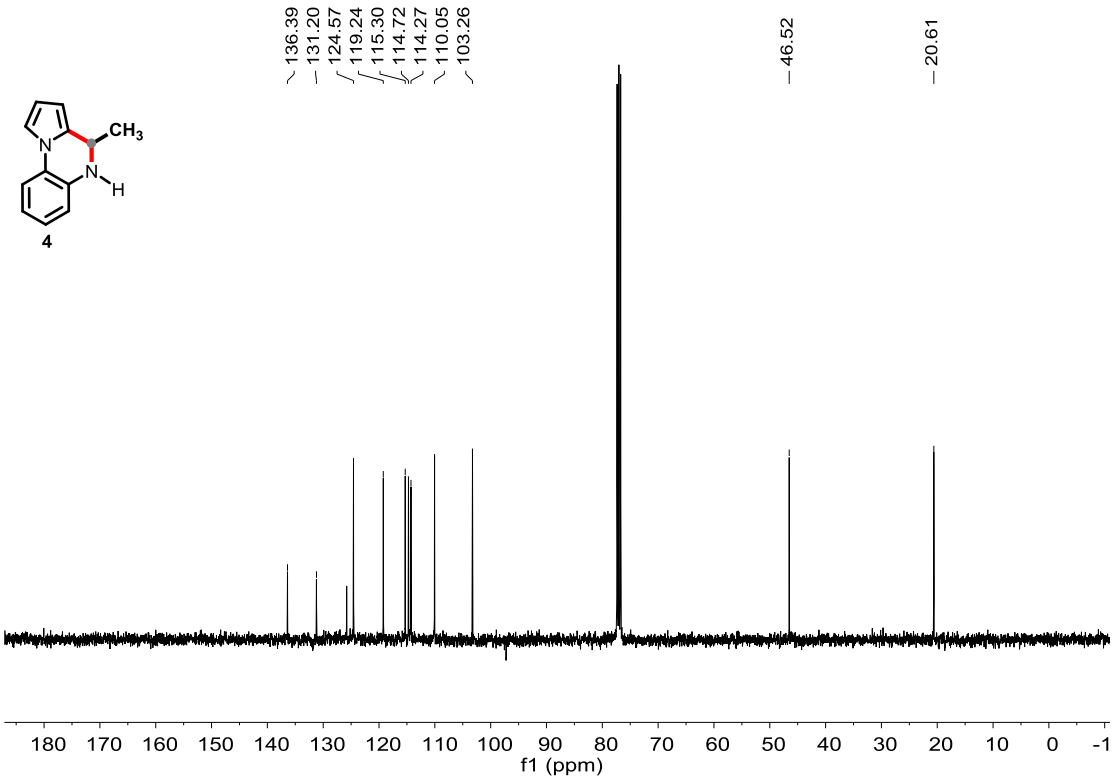

8.76
8.76
8.75
8.75
8.31
8.30
8.29
8.28
8.01
8.00
7.70
7.70
7.68
7.66
7.66
7.52
7.50
7.48
7.48
7.46
7.45
7.44
7.43
7.11
2.88
CH3
N
N
3m'
0.92
0.93
0.95
0.95
0.99
0.98
0.97
3.00
f1 (ppm)

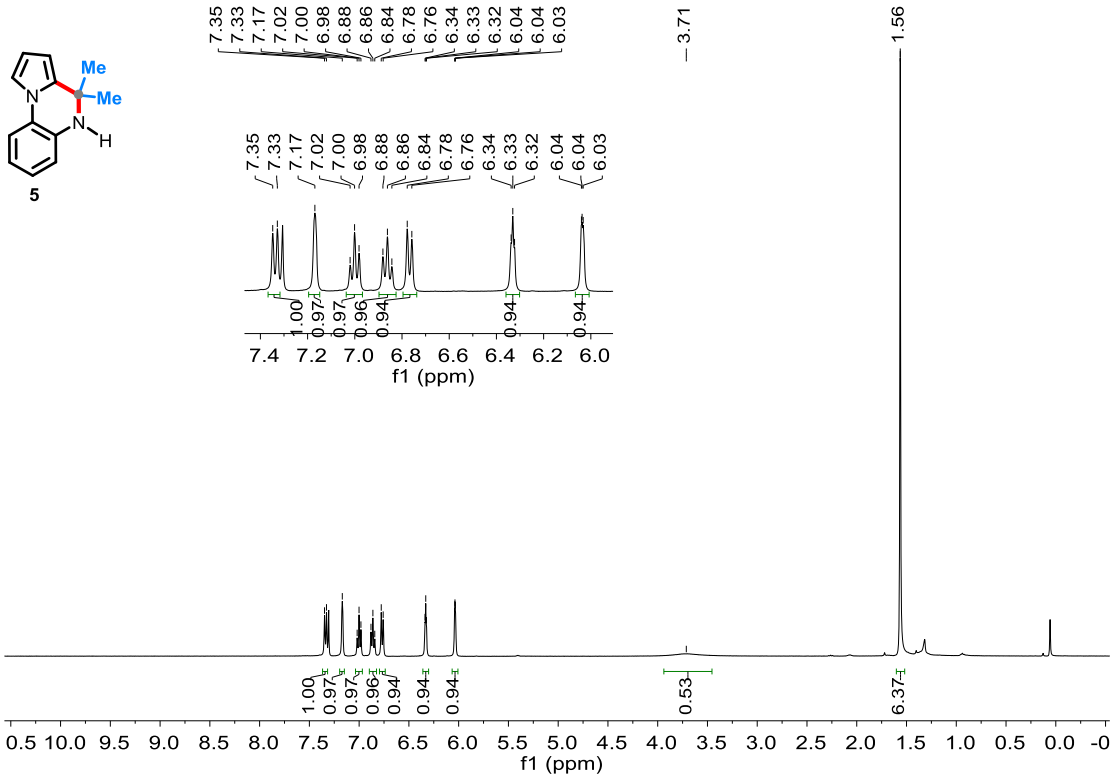

154.72
144.79
135.15
130.31
129.01
128.85
128.71
128.37
124.62
121.04
118.50
117.48
96.69
21.99
CH3
N
N
N
3m'
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

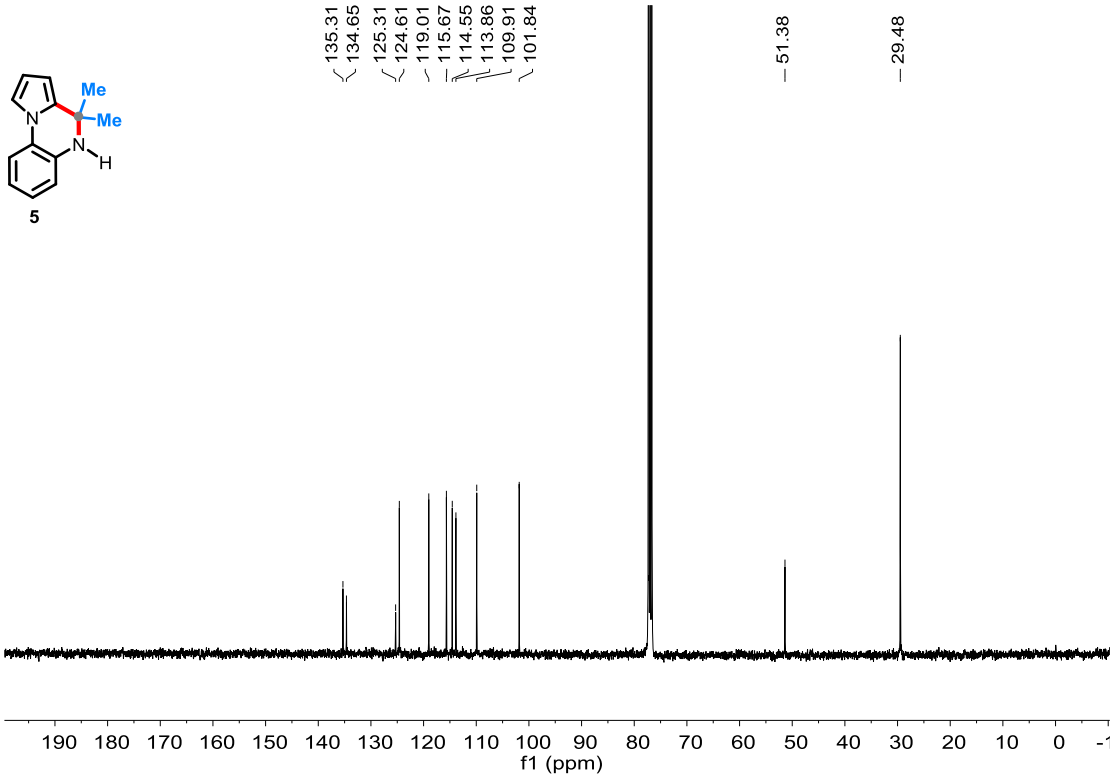

8.91
8.89
8.76
8.74
8.23
8.21
7.98
7.96
7.81
7.79
7.79
7.77
7.72
7.70
7.69
7.63
7.61
7.59
7.13
7.11
7.09
3.25
CH3
N
N
N
3n'
0.97
1.00
1.00
1.04
0.93
1.07
1.09
1.08
3.00
8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2
f1 (ppm)
0.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

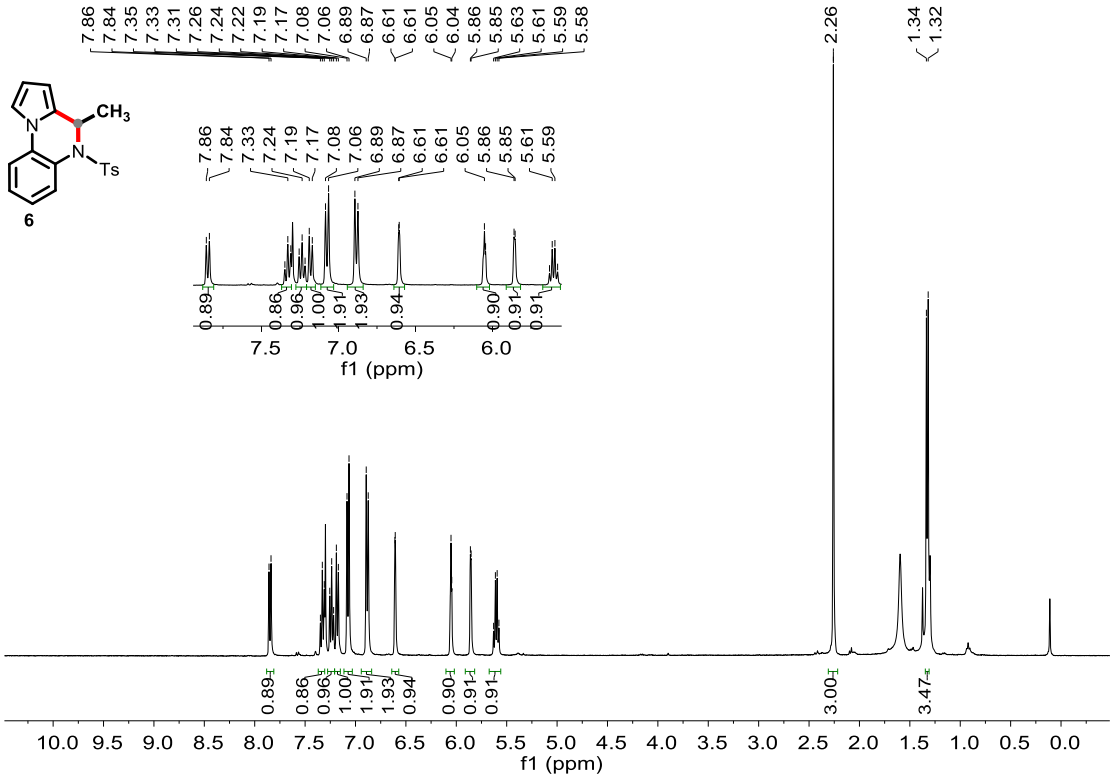

149.31
146.70
145.79
144.83
129.42
128.70
128.58
127.24
126.05
122.58
121.74
121.36
118.28
112.64
24.23
CH3
N
N
3n'
f1 (ppm)

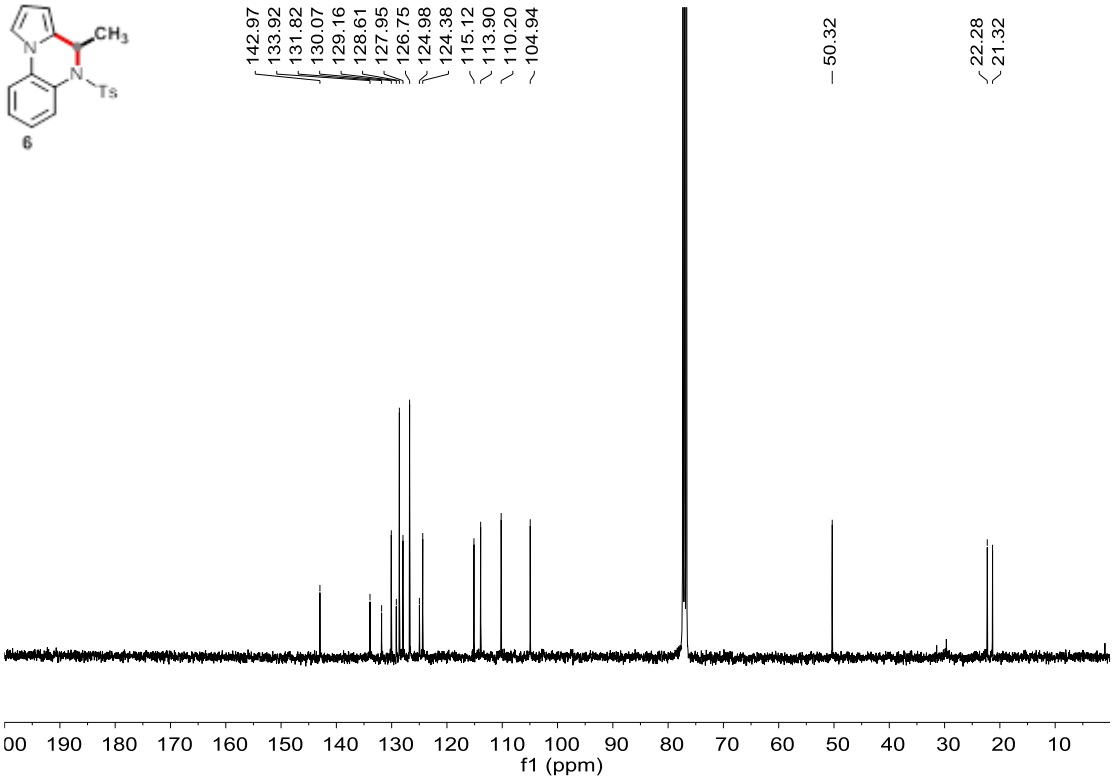

7.35
7.33
7.20
7.03
7.01
6.99
6.89
6.87
6.86
6.80
6.78
6.37
6.36
6.36
6.05
6.04
4.64
4.62
4.60
4.59
1.62
1.60
CH3
N
H
4
1.00
0.99
0.98
0.99
0.98
0.96
0.95
0.96
0.79
3.23
f1 (ppm)


136.39
131.20
124.57
119.24
115.30
114.72
114.27
110.05
103.26
46.52
20.61
CH3
N
N
H
4
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


7.35
7.33
7.17
7.02
7.00
6.98
6.88
6.86
6.84
6.78
6.76
6.34
6.33
6.32
6.04
6.04
6.03
3.71
1.56
Me
Me
N
N
H
5
1.00
0.97
0.97
0.96
0.94
0.94
0.94
0.53
6.37
7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0
f1 (ppm)
0.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)


Me
Me
N
H
5
135.31
134.65
125.31
124.61
119.01
115.67
114.55
113.86
109.91
101.84
51.38
29.48
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


CH3
N
Ts
6
7.86
7.84
7.35
7.33
7.31
7.26
7.24
7.22
7.19
7.17
7.08
7.06
6.89
6.87
6.61
6.61
6.05
6.04
5.86
5.85
5.63
5.61
5.59
5.58
2.26
1.34
1.32
0.89
0.86
0.96
1.00
1.91
1.93
0.94
0.90
0.91
0.91
3.00
3.47
7.5 7.0 6.5 6.0
f1 (ppm)
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


CH3
N
N
Ts
6
142.97
133.92
131.82
130.07
129.16
128.61
127.95
126.75
124.98
124.38
115.12
113.90
110.20
104.94
50.32
22.28
21.32
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)