Supporting Information

Contents

General Information

^{1}H NMR spectra were recorded on a Bruker AM 400 (400 MHz), a Bruker DRX 500 (500 MHz) or on a Bruker Avance 600 (600 MHz) spectrometer. Chemical shifts are expressed in parts per million (ppm, δ) downfield from tetramethylsilane (TMS) and are referenced to $CHCl_3$ (7.26 ppm) as internal standard. All coupling constants are absolute values, and J values are expressed in Hertz (Hz). The description of signals includes: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, ddd = doublet of dd, dt = doublet of triplet, td = triplet of doublet, bs = broad singlet, m = multiplet. The spectra were analyzed according to the first order. – ^{13}C NMR spectra were recorded on a Bruker AM 400 (100 MHz), a Bruker DRX 500 (125 MHz) or on a Bruker Avance 600 (150 MHz) spectrometer. Chemical shifts are expressed in parts per million (ppm, δ) downfield from tetramethylsilane (TMS) and are referenced to $CDCl_3$ (77.0 ppm) as internal standard. – MS (EI) (electron impact mass spectrometry) and MS (FAB) (fast atom bombardment): Finnigan MAT 90 (70 eV). The peaks are given as mass-to-charge ratio (m/z). The molecule peak is given as $[M]^+$. For the high-resolution mass, the following abbreviations were used: calc.= theoretical calculated mass; found = mass found in the analysis. – IR (infrared spectroscopy): FT-IR Bruker IFS 88 and Bruker alpha. IR spectra of solids were recorded in KBr or ATR technique (ATR = Attenuated Total Reflection) and as thin films on KBr for oils and liquids. The deposit of the absorption band was given in wavenumbers $\tilde{\nu}$ in cm^{-1} between 3600 cm^{-1} and 500 cm^{-1}. Band intensities were characterized as follows: vs = very strong (0 - 10% transmission (T)), s = strong (11 - 30% T), m = medium (31 - 70% T), w = weak (71 - 90% T), vw = very weak (91 - 100% T).– Routine monitoring of reactions was performed using Silica gel-coated aluminum plates (Merck, silica gel 60, F254), which were analyzed under UV-light at 254 nm. Solvent mixtures are understood as volume/volume. Solid materials were powdered. Solvents, reagents, and chemicals were purchased from Aldrich, Fluka, Carbolution, ChemPur, ABCR, TCI, and Fisher Scientific. All reactions involving moisture-sensitive reactants were executed under an argon atmosphere using oven-dried and/or flame-dried glassware. All other solvents, reagents, and chemicals were used as purchased unless stated otherwise. Air- or moisture-sensitive reactions were performed under an argon atmosphere in previously evacuated and heated glassware. Liquids were transferred with plastic syringes and steel cannula. Solids were used as powders. Reaction control was performed by thin-layer chromatography. Solvents were removed at 40 °C at the rotavapor. If not stated otherwise, crude products were purified by flash chromatography with Silica

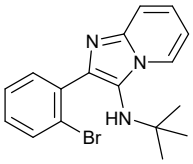
gel 60 (0.040 × .063 mm, Geduran®) (Merck), which was used as stationary phase, and solvents of p.a. quality were used as mobile phase.

CCDC 2152372 (**9d**), and 2152373 (**10a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Experimental pUC DNA relaxation assay

DNA intercalation was assessed using the pUC DNA relaxation assay. Briefly, 500 ng pUC19 DNA was dissolved in enzyme buffer (40 mM sodium phosphate, 100 mM NaCl, pH 7.4) and incubated with the respective compound for 1 h at 37^0 C in the dark. Supercoiled (sc) and open circular (OC) forms of pUC19 DNA were separated by electrophoresis in a 1% agarose gel containing GelRed (1/10 000) for 2.5 h at 90 V. The density of the bands was quantified using a Herolab gel detection system (EASY win 32).

2-(2-Bromophenyl)-*N*-(*tert.*-butyl)imidazo[1,2-*a*]pyridine-3-amine, 4



2-Aminopyridine (600 mg, 6.38 mmol, 1.00 equiv.), 2-bromobenzaldehyde (1.18 g, 744 µL, 6.38 mmol, 1.00 equiv.), *tert.*-butyl isocyanide (530 mg, 721 µL, 6.38 mmol, 1.00 equiv.) and a 1M solution of perchloric acid in methanol (64.0 mg, 638 µL, 638 µmol, 0.10 equiv.) were reacted in 10 mL methanol for 3 d. After purification *via* column chromatography (SiO_2, CH/EtOAc/NEt_3 6:1:0.01 to 1:1:0.04), GBB product **4** was obtained as a beige solid (1.83 g, 5.33 mmol, 84%).

***R*$_f$** (SiO_2, CH/EtOAc 1:1) = 0.27.

^{1}H-NMR (400 MHz, $CDCl_3$) δ [ppm] = 8.30 (dd, *J* = 6.9, 1.2 Hz, 1H, CH_{Ar}), 7.64 (ddd, *J* = 7.8, 1.5 Hz, 2H, CH_{Ar}), 7.53 (dd, *J* = 9.1, 1.1 Hz, 1H, CH_{Ar}), 7.39 (td, *J* = 7.5 , 1.3 Hz, 1H, CH_{Ar}), 7.28 – 7.09 (m, 2H, CH_{Ar}), 6.79 (td, *J* = 6.8, 1.2 Hz, 1H, CH_{Ar}), 3.21 (s, 1H, N*H*), 0.92 (s, 9H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ [ppm] = 157.0 (C_q), 142.1 (C_q), 139.3 (C_q), 137.1 (C_q), 133.2 (CH_{Ar}), 132.7 (CH_{Ar}), 129.5 (CH_{Ar}), 127.6 (CH_{Ar}), 123.8 (CH_{Ar}), 122.2 (C_q), 117.5 (CH_{Ar}), 111.5 (CH_{Ar}), 101.4 (CH_{Ar}), 55.9 (C_q), 30.1 (3C, CH_3).

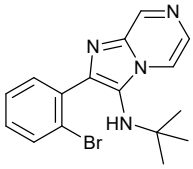
IR (ATR) $\tilde{\nu}$ [cm^{-1}]= 3228 (w), 2962 (w), 2861 (w), 1629 (w), 1553 (w), 1500 (w), 1468 (w), 1431 (w), 1384 (m), 1353 (m), 1337 (s), 1271 (w), 1222 (s), 1205 (m), 1197 (m), 1142 (w), 1024 (m), 946 (w), 918 (w), 809 (w), 752 (vs), 738 (vs), 727 (s), 715 (m), 700 (s), 674 (w), 649 (m), 608 (m), 582 (w), 571 (w), 524 (w), 486 (w), 465 (w), 416 (m).

FAB-MS *m/z* (%): 347 (20), 346 (99) [M(^{81}Br) + H]$^+$, 345 (54), 344 [M(^{79}Br) + H]$^+$ (100), 343 (36), 290 (10), 289 (26), 288 (30), 287 (25), 286 (20), 261 (13), 259 (10), 208 (5), 181 (12), 147 (8).

HRMS-FAB (*m/z*): [M + H]$^+$ calcd. for $C_{17}H_{19}N_3{}^{79}Br_1$, 344.0757; found, 344.0759.

Additional information on the chemical synthesis is available via Chemotion repository: https://dx.doi.org//reaction/SA-FUHFF-UHFFFADPSC-ZHNWMBYOQO-UHFFFADPSC-NUHFF-NUHFF-NUHFF-ZZZ
Additional information on the analysis of the target compound is available via Chemotion repository: https://dx.doi.org//ZHNWMBYOQOJQTI-UHFFFAOYSA-N.1

2-(2-Bromophenyl)-*N*-(*tert.*-butyl)imidazo[1,2-*a*]pyrazine-3-amine, 5



2-Aminopyrazine (600 mg, 6.31 mmol, 1.00 equiv.), 2-bromobenzaldehyde (1.17 mg, 736 µL, 6.31 mmol, 1.00 equiv.), *tert.*-butyl isocyanide (525 mg, 714 µL, 6.31 mmol, 1.00 equiv.) and a 1M solution of perchloric acid in methanol (63.4 mg, 631 µL, 6.31 mmol, 0.10 equiv.) were reacted in 10 mL methanol for 3 d. After purification *via* column chromatography (SiO_2, CH/EtOAc/NEt_3 6:1:0.01 to 1:2:0.04), GBB product **5** was obtained as a beige solid (1.70 g, 4.92 mmol, 78%).

***R*$_f$** (SiO_2, CH/EtOAc 1:2) = 0.21.

^{1}H-NMR (400 MHz, $CDCl_3$) δ [ppm] = 9.00 (d, *J* = 1.5 Hz, 1H, C*H*$_{Ar}$), 8.21 (dd, *J* = 4.7, 1.5 Hz, 1H, C*H*$_{Ar}$), 7.88 (d, *J* = 4.7 Hz, 1H, C*H*$_{Ar}$), 7.66 (dd, *J* = 8.0, 1.2 Hz, 1H, C*H*$_{Ar}$), 7.62 (dd, *J* = 7.7, 1.8 Hz, 1H, C*H*$_{Ar}$), 7.43 (td, *J* = 7.5, 1.2 Hz, 1H, C*H*$_{Ar}$), 7.32 – 7.27 (m, 1H, C*H*$_{Ar}$), 2.97 – 2.85 (s, 1H, N*H*), 0.93 (s, 9H, C*H*$_3$).

^{13}C-NMR (101 MHz, $CDCl_3$) δ [ppm] = 143.7 (CH_{Ar}), 142.0 (C_q), 137.4 (C_q), 135.9 (C_q), 133.1 (CH_{Ar}), 132.9 (CH_{Ar}), 130.2 (CH_{Ar}), 129.1 (CH_{Ar}), 127.8 (CH_{Ar}), 126.3 (C_q), 122.7 (C_q), 116.7 (CH_{Ar}), 56.4 (C_q), 30.1 (3C, CH_3).

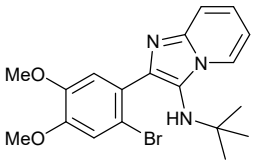
IR (ATR) $\tilde{\upsilon}$ [cm^{-1}] = 3234 (w), 2962 (m), 1666 (m), 1596 (w), 1538 (w), 1488 (w), 1463 (m), 1433 (m), 1388 (m), 1362 (m), 1343 (m), 1311 (w), 1290 (w), 1209 (m), 1160 (w), 1026 (m), 916 (w), 814 (m), 759 (m), 710 (m), 658 (w), 607 (m), 465 (w), 438 (w), 417 (m).

FAB-MS *m/z* (%): 347 [M(^{81}Br) + H]$^+$ (98), 346 [M(^{81}Br)]$^+$ (49), 345 [M(^{79}Br) + H]$^+$ (100), 344 [M(^{79}Br)]$^+$ (24), 290 [M(^{81}Br) – tBu + H]$^+$ (31), 289 [M(^{81}Br) – tBu]$^+$ (24), 288 [M(^{79}Br) – tBu + H]$^+$ (27).

HRMS-FAB (*m/z*): [M + H]$^+$ calcd. for $C_{16}H_{18}N_4{}^{79}Br$, 345.0715; found, 345.0716.

Additional information on the chemical synthesis is available via Chemotion repository: https://dx.doi.org//reaction/SA-FUHFF-UHFFFADPSC-FDKYXFKVWI-UHFFFADPSC-NUHFF-NUHFF-NUHFF-ZZZ
Additional information on the analysis of the target compound is available via Chemotion repository: https://dx.doi.org//FDKYXFKVWISCIL-UHFFFAOYSA-N.1

2-(2-Bromo-4,5-dimethoxyphenyl)-*N*-(*tert.*-butyl)imidazo[1,2-*a*]pyridine-3-amine, 6



2-Aminopyridine (600 mg, 6.38 mmol, 1.00 equiv.), 2-bromo-4,5-dimethoxybenzaldehyde (1.56 g, 6.38 mmol, 1.00 equiv.), *tert.*-butyl isocyanide (530 mg, 721 µL, 6.38 mmol, 1.00 equiv) and a 1M solution of perchloric acid in methanol (64.0 mg, 638 µL, 638 µmol, 0.10 equiv) were reacted in 10 mL methanol for 3 d. After purification *via* column chromatography (SiO_2, CH/EtOAc/NEt_3 6:1:0.01 to 1:2:0.04), GBB product **6** was obtained as a beige solid (1.79 g, 4.44 mmol, 70%).

R_f (SiO_2, CH/EtOAc 1:2) = 0.21.

^{1}H-NMR (400 MHz, $CDCl_3$) δ [ppm] = 8.30 (dt, *J* = 6.9, 1.2 Hz, 1H, C*H*$_{Ar}$), 7.51 (dd, *J* = 9.0, 1.1 Hz, 1H, C*H*$_{Ar}$), 7.17 (s, 1H, C*H*$_{Ar}$), 7.16 – 7.11 (m, 1H, C*H*$_{Ar}$), 7.06 (s, 1H, C*H*$_{Ar}$), 6.78 (td, *J* = 6.7, 1.2 Hz, 1H, C*H*$_{Ar}$), 3.92 – 3.85 (m, 6H, OC*H*$_3$), 2.01 (s, 1H, N*H*), 0.94 (s, 9H, C*H*$_3$).

^{13}C-NMR (101 MHz, $CDCl_3$) δ [ppm] = 149.5 (C_q), 148.6 (C_q), 142.0 (C_q), 139.2 (C_q), 129.3 (C_q), 124.6 (C_q), 124.2 (CH_{Ar}), 123.8 (CH_{Ar}), 117.4 (CH_{Ar}), 115.1 (CH_{Ar}), 115.0 (CH_{Ar}), 112.8 (C_q), 111.4 (CH_{Ar}), 56.3 (CH_3), 55.9 (CH_3), 30.1 (3C, CH_3), 27.0 (C_q).

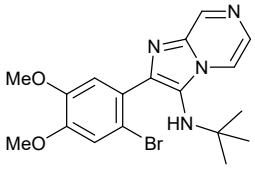
IR (ATR) $\tilde{\upsilon}$ [cm^{-1}] = 3344 (vw), 2964 (w), 1740 (w), 1684 (w), 1631 (w), 1604 (w), 1503 (s), 1462 (m), 1440 (m), 1405 (m), 1341 (m), 1249 (m), 1205 (s), 1172 (m), 1026 (m), 952 (w), 912 (w), 861 (w), 833 (w), 756 (m), 728 (m), 642 (w), 599 (w), 498 (w), 418 (w).

FAB-MS *m/z* (%): 406 $[M(^{81}Br) + H]^+$ (99), 405 $[M(^{81}Br)]^+$ (63), 404 $[M(^{79}Br) + H]^+$ (100), 403 $[M(^{79}Br)]^+$ (39), 349 $[M(^{81}Br) – tBu + H]^+$ (12), 348 $[M(^{81}Br) – tBu]^+$ (21), 347 $[M(^{79}Br) – tBu + H]^+$ (12), 346 $[M(^{79}Br) – tBu]^+$ (18).

HRMS-FAB (*m/z*): $[M + H]^+$ calcd. for $C_{19}H_{23}O_2N_3{}^{79}Br$, 404.0974; found, 404.0972.

Additional information on the chemical synthesis is available via Chemotion repository: https://dx.doi.org//reaction/SA-FUHFF-UHFFFADPSC-GAUNOMJAIR-UHFFFADPSC-NUHFF-NUHFF-NUHFF-ZZZ.1
Additional information on the analysis of the target compound is available via Chemotion repository: https://dx.doi.org//GAUNOMJAIRSHHA-UHFFFAOYSA-N.2

2-(2-Bromo-4,5-dimethoxyphenyl)-*N*-(*tert.*-butyl)imidazo[1,2-*a*]pyrazine-3-amine, 7



2-Aminopyrazine (600 mg, 6.31 mmol, 1.00 equiv.), 2-bromo-4,5-dimethoxybenzaldehyde (1.55 g, 6.31 mmol, 1.00 equiv.), *tert.*-butyl isocyanide (530 mg, 721 µL, 6.31 mmol, 1.00 equiv.) and a 1M solution of perchloric acid in methanol (63.4 mg, 631 µL, 631 µmol, 0.10 equiv.) were reacted in 10 mL methanol for 3 d. After purification *via* column chromatography (SiO_2, CH/EtOAc/NEt_3 6:1:0.01 to 1:2:0.04), GBB product **7** was obtained as a beige solid (1.86 g, 4.59 mmol, 73%).

R_f (SiO_2, CH/EtOAc 1:1) = 0.40.

^{1}H-NMR (400 MHz, $CDCl_3$) δ [ppm] = 8.98 (d, *J* = 1.5 Hz, 1H, C*H*$_{Ar}$), 8.20 (dd, *J* = 4.7, 1.5 Hz, 1H, C*H*$_{Ar}$), 7.87 (d, *J* = 4.7 Hz, 1H, C*H*$_{Ar}$), 7.13 (s, 1H, C*H*$_{Ar}$), 7.08 (s, 1H, C*H*$_{Ar}$), 3.92 (s, 3H, OC*H*$_3$), 3.90 (s, 3H, OC*H*$_3$), 3.32 (s, 1H, N*H*), 0.94 (s, 9H, C*H*$_3$).

^{13}C-NMR (101 MHz, $CDCl_3$) δ [ppm] = 150.0 (C_q), 148.8 (C_q), 141.9 (C_q), 137.4 (C_q), 132.7 (CH_{Ar}), 129.1 (CH_{Ar}), 128.1 (C_q), 126.1 (C_q), 116.6 (CH_{Ar}), 115.2 (CH_{Ar}), 114.9 (CH_{Ar}), 112.8 (C_q), 60.5 (C_q), 56.4 (CH_3), 56.3 (CH_3), 30.1 (3C, CH_3).

IR (ATR) $\tilde{\upsilon}$ [cm^{-1}] = 3334 (vw), 2962 (vw), 1736 (vw), 1604 (w), 1537 (vw), 1501 (w), 1462 (w), 1441 (w), 1408 (w), 1365 (w), 1349 (w), 1249 (w), 1203 (m), 1173 (w), 1018 (w), 952 (w), 858 (w), 823 (w), 779 (w), 699 (vw), 646 (w), 611 (w), 584 (vw), 421 (w).

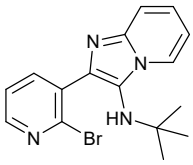
FAB-MS *m/z* (%): 407 $[M(^{81}Br) + H]^+$ (97), 406 $[M(^{81}Br)]^+$ (62), 405 $[M(^{79}Br) + H]^+$ (100), 404 $[M(^{79}Br)]^+$ (43).

HRMS-FAB (*m/z*): $[M + H]^+$ calcd. for $C_{18}H_{22}O_2N_4{}^{79}Br$, 405.0926; found, 405.0928.

Additional information on the chemical synthesis is available via Chemotion repository: https://dx.doi.org//reaction/SA-FUHFF-UHFFFADPSC-BXFGUOURKQ-UHFFFADPSC-NUHFF-NUHFF-NUHFF-ZZZ.1

Additional information on the analysis of the target compound is available via Chemotion repository: https://dx.doi.org//BXFGUOURKQXMMO-UHFFFAOYSA-N.2

2-(2-Bromopyridine)-*N*-(*tert.*-butyl)imidazo[1,2-*a*]pyridine-3-amine, 8



2-Aminopyridine (300 mg, 3.19 mmol, 1.00 equiv.), 2-bromo-3-pyridinecarboxaldehyde (593 mg, 0.38 mL, 3.19 mmol, 1.00 equiv.), *tert.*-butyl isocyanide (265 mg, 0.36 mL, 3.19 mmol, 1.00 equiv.) and glacial acetic acid (383 mg, 0.37 mL, 6.37 mmol, 2.00 equiv.) were reacted in 10 mL methanol for 3 d. After purification *via* column chromatography (SiO_2, CH/EtOAc/NEt_3 6:1:0.01 to 1:2:0.04) GBB product **8** was obtained as a beige solid (223 mg, 0.65 mmol, 20%).

***R*$_f$** (SiO_2, CH/EtOAc 1:2) = 0.13.

^{1}H-NMR (400 MHz, $CDCl_3$) δ [ppm] = 8.39 (dd, *J* = 4.7, 2.0 Hz, 1H, C*H*$_{Ar}$), 8.32 (dt, *J* = 6.9, 1.2 Hz, 1H, C*H*$_{Ar}$), 8.00 (dd, *J* = 7.6, 2.0 Hz, 1H, C*H*$_{Ar}$), 7.52 (d, *J* = 9.1 Hz, 1H, C*H*$_{Ar}$), 7.38 (dd, *J* = 7.6, 4.7 Hz, 1H, C*H*$_{Ar}$), 7.19 (ddd, *J* = 9.0, 6.6, 1.3 Hz, 1H, C*H*$_{Ar}$), 6.82 (td, *J* = 6.8, 1.1 Hz, 1H, C*H*$_{Ar}$), 3.22 (s, 1H, N*H*), 0.93 (s, 9H, C*H*$_3$). Spectrum contains signals of H-grease.

^{13}C-NMR (101 MHz, $CDCl_3$) δ [ppm] = 149.4 (CH_{Ar}), 142.5 (C_q), 141.7 (C_q), 141.4 (CH_{Ar}), 137.1 (C_q), 134.8 (C_q), 125.0 (C_q), 124.9 (CH_{Ar}), 123.9 (CH_{Ar}), 122.9 (CH_{Ar}), 117.5 (CH_{Ar}), 111.9 (CH_{Ar}), 55.9 (C_q), 30.2 (3C, CH_3).

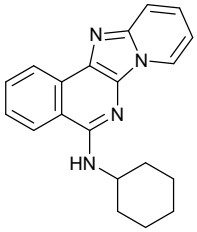
IR (ATR) $\tilde{\upsilon}$ [cm^{-1}] = 3227 (vw), 2961 (vw), 1647 (vw), 1550 (w), 1501 (w), 1398 (w), 1376 (w), 1352 (w), 1337 (w), 1224 (w), 1201 (w), 1151 (vw), 1119 (vw), 1047 (w), 918 (vw), 841 (vw), 801 (w), 760 (w), 740 (w), 726 (w), 710 (w), 684 (w), 611 (w), 524 (w), 444 (vw), 414 (w).

FAB-MS *m/z* (%): 347 [M(^{81}Br) + H]$^+$ (97), 346 [M(^{81}Br)]$^+$ (57), 345 [M(^{79}Br) + H]$^+$ (100), 344 [M(^{79}Br)]$^+$ (39), 290 [M(^{81}Br) – tBu + H]$^+$ (25), 289 [M(^{81}Br) – tBu]$^+$ (22), 288 [M(^{79}Br) – tBu + H]$^+$ (24), 287 [M(^{79}Br) – tBu]$^+$ (12).

HRMS-FAB (*m/z*): [M + H]$^+$ calcd. for $C_{16}H_{18}N_4{}^{79}Br$, 345.0715; found, 345.0716.

Additional information on the chemical synthesis is available via Chemotion repository: https://dx.doi.org//reaction/SA-FUHFF-UHFFFADPSC-HQVPHYCHTW-UHFFFADPSC-NUHFF-NUHFF-NUHFF-ZZZ.1
Additional information on the analysis of the target compound is available via Chemotion repository: https://dx.doi.org//HQVPHYCHTWJXNH-UHFFFAOYSA-N.2

***N*-(Cyclohexyl)pyrido[2',1':2,3]imidazo[4,5-c]isoquinolin-5-amine, 9a**



GBB-product **4** (200 mg, 0.58 mmol, 1.00 equiv), cyclohexyl isocyanide (95.1 mg, 0.11 mL, 0.87 mmol, 1.5 equiv), potassium acetate (171 mg, 1.74 mmol, 3.00 equiv), Pd-Peppsi (19.8 mg, 0.03 mmol, 0.05 equiv) and XPhos (27.7 mg, 0.06 mmol, 0.10 equiv) were reacted in 3 mL DMF for 18 h at 120 °C. After purification *via* column chromatography (SiO_2, CH/EtOAc/NEt_3 20:1:0.05 to 2:1:0.05) insertion product **9a** was obtained as a yellow solid (172 mg, 0.54 mmol, 94%).

***R*$_f$** (SiO_2, CH/EtOAc 2:1) =0.11.

^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm] = 8.64 (dd, *J* = 8.1, 1.2 Hz, 1H, C*H*$_{Ar}$), 8.59 (dt, *J* = 6.9, 1.3 Hz, 1H, C*H*$_{Ar}$), 7.89 (d, *J* = 8.3, 1H, C*H*$_{Ar}$), 7.75 (ddd, *J* = 8.1, 7.0, 1.0 Hz, 1H, C*H*$_{Ar}$), 7.73-7.70 (m, 1H, CH$_{Ar}$), 7.52 (ddd, *J* = 8.4, 7.0, 1.3 Hz, 1H, C*H*$_{Ar}$), 7.32-7.22 (m, 1H, C*H*$_{Ar}$), 6.87 (td, *J* = 6.7, 1.1 Hz, 1H, C*H*$_{Ar}$), 5.37 (d, *J* = 7.2 1H, N*H*), 4.29 (dt, *J* = 7.0, 3.8 Hz, 1H, C*H*), 2.27-2.21 (m, 2H, C*H*$_2$), 1.84 (dt, *J* = 13.5, 3.9 Hz, 2H, C*H*$_2$), 1.72 (dt, *J* = 12.8, 3.9 Hz, 2H, C*H*$_2$), 1.58-1.47 (m, 2H, C*H*$_2$), 1.38-1.34 (m, 2H, C*H*$_2$).

^{13}C NMR (101 MHz, $CDCl_3$) δ [ppm] = 151.5 (C$_q$), 143.4 (C$_q$), 134.6 (C$_q$), 130.9 (C$_q$), 130.4 (CH$_{Ar}$), 126.3 (CH$_{Ar}$), 125.8 (CH$_{Ar}$), 124.5 (C$_q$), 123.3 (CH$_{Ar}$), 123.2 (CH$_{Ar}$), 122.7 (CH$_{Ar}$), 119.0 (C$_q$), 117.3 (CH$_{Ar}$), 111.2 (CH$_{Ar}$), 50.3 (CH), 33.3 (2C, CH$_2$), 26.1 (CH$_2$), 25.3 (2C, CH$_2$).

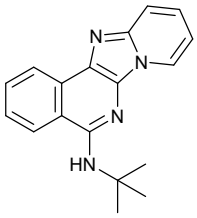
IR (ATR) $\tilde{\upsilon}$ [cm^{-1}] 3273 (vw), 2923 (w), 2850 (w), 1623 (w), 1583 (w), 1540 (w), 1506 (m), 1449 (w), 1420 (w), 1378 (w), 1348 (w), 1316 (w), 1255 (w), 1144 (w), 1109 (w), 1026 (w), 922 (w), 743 (w), 729 (m), 669 (w), 642 (w), 520 (w), 443 (vw), 420 (vw).

FAB-MS *m/z* (%): 317 [M + H]$^+$ (100), 316 [M]$^+$ (83), 234 [M – C_6H_{11} + H]$^+$ (13).

HRMS-FAB (*m/z*): [M + H]$^+$ calcd. for $C_{20}H_{21}N_4$, 317.1766; found, 317.1767.

Additional information on the chemical synthesis is available via Chemotion repository: https://dx.doi.org//reaction/SA-FUHFF-UHFFFADPSC-KESLSXGLUL-UHFFFADPSC-NUHFF-NUHFF-NUHFF-ZZZ.1
Additional information on the analysis of the target compound is available via Chemotion repository: https://dx.doi.org//KESLSXGLULXVFT-UHFFFAOYSA-N.2

***N*-(*tert*-Butyl)pyrido[2',1':2,3]imidazo[4,5-c]isoquinolin-5-amine, 9b**



GBB-product **4** (200 mg, 0.58 mmol, 1.00 equiv), tert-butyl isocyanide (72.5 mg, 0.10 mL, 0.87 mmol, 1.5 equiv), potassium acetate (171 mg, 1.74 mmol, 3.00 equiv), Pd-Peppsi-iPr (19.8 mg, 0.03 mmol, 0.05 equiv) and XPhos (27.7 mg, 0.06 mmol, 0.10 equiv) were reacted in 3 mL DMF for 18 h at 120 °C. After purification *via* column chromatography (SiO_2,

CH/EtOAc/NEt_3 20:1:0.05 to 2:1:0.05) insertion product **9b** was obtained as a yellow solid (40.8 mg, 0.14 mmol, 24%).

R_f (SiO_2, CH/EtOAc 2:1) = 0.12.

^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm] = 8.65 (dt, *J* = 8.1, 1.1 Hz, 1H, C*H*$_{Ar}$), 8.60 (dt, *J* = 6.8, 1.3 Hz, 1H, C*H*$_{Ar}$), 7.84 (dt, *J* = 8.4, 0.9 Hz, 1H, C*H*$_{Ar}$), 7.78 (ddd, *J* = 8.1, 7.0, 1.1 Hz, 1H, C*H*$_{Ar}$), 7.70 (dt, *J* = 9.2, 1.1 Hz, 1H, C*H*$_{Ar}$), 7.54 (ddd, *J* = 8.4, 7.0, 1.3 Hz, 1H, C*H*$_{Ar}$), 7.27 (ddd, *J* = 9.2, 6.6, 1.3 Hz, 1H, C*H*$_{Ar}$), 6.87 (td, *J* = 6.7, 1.1 Hz, 1H, C*H*$_{Ar}$), 5.33 (s, 1H, N*H*), 1.69 (s, 9H, C*H*$_3$).

^{13}C NMR (126 MHz, $CDCl_3$) δ [ppm] = 151.3 (C_q), 143.8 (C_q), 134.4 (C_q), 131.4 (C_q), 130.2 (CH_{Ar}), 126.0 (CH_{Ar}), 125.7 (CH_{Ar}), 125.0 (C_q), 123.3 (CH_{Ar}), 123.2 (CH_{Ar}), 122.8 (CH_{Ar}), 119.5 (C_q), 117.7 (CH_{Ar}), 111.0 (CH_{Ar}), 52.3 (C_q), 29.2 (3C, CH_3).

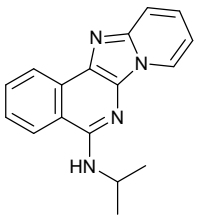
IR (ATR) $\tilde{\upsilon}$ [cm^{-1}] = 3312 (w), 3047 (w), 2962 (m), 2924 (m), 2870 (w), 2856 (w), 1664 (w), 1632 (w), 1621 (m), 1582 (m), 1560 (m), 1536 (m), 1504 (vs), 1483 (m), 1449 (s), 1421 (vs), 1378 (s), 1346 (vs), 1302 (vs), 1271 (s), 1258 (vs), 1225 (vs), 1221 (vs), 1205 (vs), 1154 (m), 1147 (s), 1123 (m), 1082 (m), 1071 (s), 1028 (s), 1004 (m), 938 (m), 929 (m), 860 (w), 823 (m), 802 (m), 788 (m), 765 (vs), 741 (vs), 732 (vs), 707 (s), 694 (m), 669 (vs), 650 (s), 635 (s), 611 (m), 591 (m), 565 (m), 521 (vs), 486 (m), 439 (vs), 422 (s), 404 (s), 381 (vs).

FAB-MS *m/z* (%): 365 (8), 292 (22), 291 (100), 290 (83), 289 (6), 275 (7), 236 (6), 235 (26), 234 (32), 133 (16).

HRMS-FAB (*m/z*): $[M + H]^+$ calcd. for $C_{18}H_{19}N_4$, 291.1604; found, 291.1602.

Additional information on the chemical synthesis is available via Chemotion repository: https://dx.doi.org//reaction/SA-FUHFF-UHFFFADPSC-SFYOEOMJOC-UHFFFADPSC-NUHFF-NUHFF-NUHFF-ZZZ.1
Additional information on the analysis of the target compound is available via Chemotion repository: https://dx.doi.org//SFYOEOMJOCGUAE-UHFFFAOYSA-N.2

***N*-(Isopropyl)pyrido[2',1':2,3]imidazo[4,5-c]isoquinolin-5-amine, 9c**



GBB product **4** (200 mg, 0.58 mmol, 1.00 equiv), isopropyl isocyanide (60.22 mg, 0.08 mL, 0.87 mmol, 1.5 equiv), potassium acetate (171 mg, 1.74 mmol, 3.00 equiv), Pd- Peppsi (19.8 mg, 0.03 mmol, 0.05 equiv) and XPhos (27.7 mg, 0.06 mmol, 0.10 equiv) were reacted in 3 mL DMF for 18 h at 120 °C. After purification *via* column chromatography (SiO_2, CH/EtOAc/NEt_3 20:1:0.05 to 2:1:0.05) insertion product **9c** was obtained as a yellow solid (43 mg, 0.16 mmol, 27%).

R_f (SiO_2, CH/EtOAc 2:1) = 0.14.

^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm] = 8.63 (dd, *J* = 8.4, 0.9 Hz, 1H, CH_{Ar}), 8.59 (dt, *J* = 6.8, 1.2 Hz, 1H, CH_{Ar}), 7.89 (dt, *J* = 8.4, 0.9 Hz, 1H, CH_{Ar}), 7.76 (ddd, *J* = 8.1, 7.0, 1.1 Hz, 1H, CH_{Ar}), 7.67 (dt, *J* = 9.2, 1.1z Hz, 1H, CH_{Ar}), 7.50 (ddd, *J* = 8.4, 7.0, 1.4 Hz, 1H, CH_{Ar}), 7.23 (ddd, *J* = 9.2, 6.6, 1.4 Hz, 1H, CH_{Ar}), 6.82 (td, *J* = 6.7, 1.1 Hz, 1H, CH_{Ar}), 5.27 (d, *J* = 7.0 Hz, 1H, N*H*), 4.60 (h, *J* = 6.5 Hz 1H, C*H*), 1.40 (d, *J* = 6.5 Hz, 6H, CH_3).

^{13}C NMR (126 MHz, $CDCl_3$) δ [ppm] = 151.3 (C_q), 143.9 (C_q), 134.7 (C_q), 131.4 (C_q), 130.3 (CH_{Ar}), 125.7 (CH_{Ar}), 125.5 (CH_{Ar}), 125.5 (C_q), 123.2 (CH_{Ar}), 123.0 (CH_{Ar}), 122.7 (CH_{Ar}), 118.9 (Cq), 117.6 (CH_{Ar}), 110.7 (CH_{Ar}), 43.2 (C_q), 23.0 (2C, CH_3).

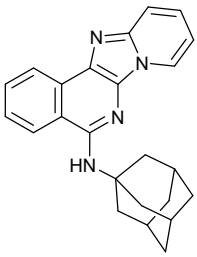
IR (ATR) $\tilde{\upsilon}$ [cm^{-1}] = 3276 (w), 3054 (w), 2972 (w), 2953 (w), 2925 (w), 2868 (w), 1632 (w), 1622 (m), 1581 (m), 1562 (m), 1541 (s), 1504 (vs), 1451 (m), 1438 (m), 1418 (s), 1380 (s), 1353 (s), 1316 (m), 1293 (s), 1279 (m), 1254 (vs), 1220 (m), 1180 (m), 1167 (m), 1160 (m), 1143 (m), 1133 (m), 1120 (m), 1082 (m), 1068 (m), 1027 (m), 1000 (w), 963 (w), 943 (w), 926 (w), 888 (w), 877 (w), 853 (w), 844 (w), 823 (w), 772 (vs), 754 (w), 739 (vs), 730 (vs), 713 (s), 693 (m), 671 (s), 643 (s), 613 (m), 589 (m), 565 (m), 521 (vs), 506 (m), 475 (m), 453 (m), 446 (m), 433 (m), 418 (s), 399 (s), 377 (s).

FAB-MS *m/z* (%): 278 (19), 277 $[M + H]^+$ (100), 276 (78), 275 (9), 261 (15), 235 (13), 234 (14), 233 (5), 219 (5), 138 (5), 137 (7), 136 (21), 133 (12), 107 (8), 105 (5), 91 (12), 90 (9), 89 (9).

HRMS-FAB (*m/z*): $[M + H]^+$ calcd. for $C_{17}H_{17}N_4$, 277.1448; found, 277.1448.

Additional information on the chemical synthesis is available via Chemotion repository: https://dx.doi.org//reaction/SA-FUHFF-UHFFFADPSC-NNQKMYYBCP-UHFFFADPSC-NUHFF-NUHFF-NUHFF-ZZZ
Additional information on the analysis of the target compound is available via Chemotion repository: https://dx.doi.org//NNQKMYYBCPGPGY-UHFFFAOYSA-N

***N*-((1s,3s)-Adamantan-1-yl)pyrido[2'1':2,3]imidazo[4,5-c]isoquinolin-5-amine, 9d**



GBB-product **4** (200 mg, 0.58 mmol, 1.00 equiv), 1-isocyanoadamantane (141 mg, 0.87 mmol, 1.5 equiv), potassium acetate (171 mg, 1.74 mmol, 3.00 equiv), Pd- Peppsi (19.8 mg, 0.03 mmol, 0.05 equiv) and XPhos (27.7 mg, 0.06 mmol, 0.10 equiv) were reacted in 3 mL DMF for 18 h at 120 °C. After purification *via* column chromatography (SiO_2, CH/EtOAc/NEt_3 20:1:0.05 to 2:1:0.05) insertion product **9d** was obtained as a yellow solid (144 mg, 0.16 mmol, 67%).

R_f (SiO_2, CH/EtOAc 2:1) = 0.28.

^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm] = 8.63 (dd, *J* = 8.1, 1.3 Hz, 1H, CH_{Ar}), 8.53 (dt, *J* = 7.0, 1.3 Hz, 1H, CH_{Ar}), 7.84 (d, *J* = 8.3 Hz, 1H, CH_{Ar}), 7.77 (ddd, *J* = 8.1, 6.9, 1.0 Hz 1H, CH_{Ar}), 7.68 (dt, *J* = 9.2, 1.3 Hz, 1H, CH_{Ar}), 7.53 (ddd, *J* = 8.4, 7.0, 1.3 Hz, 1H, CH_{Ar}), 7.25 (ddd, *J* = 9.8, 6.6, 1.4 Hz, 1H, CH_{Ar}), 6.86 (td, *J* = 6.6, 1.1 Hz, 1H, CH_{Ar}), 5.18 (s, 1H, N*H*), 2.4 (d, *J* = 2.9 Hz, 6H, CH_2), 2.21 (s, 3H, C*H*), 1.86-1.78 (m, 6H, CH_2).

^{13}C NMR (126 MHz, $CDCl_3$) δ [ppm] = 151.0 (C_q), 143.9 (C_q), 134.3 (C_q), 131.5 (C_q), 130.1 (CH_{Ar}), 125.7 (CH_{Ar}), 125.5 (CH_{Ar}), 125.2 (C_q), 123.2 (CH_{Ar}), 123.1 (CH_{Ar}), 122.8 (CH_{Ar}), 119.4 (C_q), 117.8 (CH_{Ar}), 110.9 (CH_{Ar}), 52.9 (C_q), 42.0 (3C, CH_2), 37.0 (3C, CH_2), 29.9 (3C, CH).

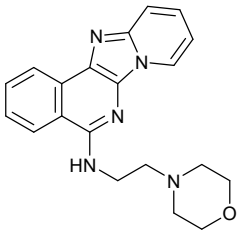
IR (ATR) $\tilde{\upsilon}$ [cm^{-1}] = 3384 (w), 3274 (w), 3080 (w), 2902 (vs), 2861 (m), 2846 (s), 1632 (w), 1623 (w), 1584 (s), 1561 (s), 1536 (m), 1509 (vs), 1451 (m), 1421 (s), 1381 (m), 1347 (vs), 1302 (vs), 1272 (s), 1258 (m), 1241 (s), 1133 (m), 1095 (m), 943 (w), 936 (w), 764 (s), 744 (vs), 734 (vs), 705 (m), 669 (s), 637 (m), 516 (s), 388 (m).

FAB-MS *m/z* (%): 370 (23), 369 (91), 368 $[M + H]^+$ (100), 367 (15), 234 (7), 135 (17), 93 (5).

HRMS-FAB (*m/z*): $[M]^+$ calcd. for $C_{24}H_{24}N_4$, 368.1995; found, 368.1997.

Additional information on the chemical synthesis is available via Chemotion repository: https://dx.doi.org//reaction/SA-FUHFF-UHFFFADPSC-RURBSASDZI-UHFFFADPSC-NUHFF-NUHFF-NUHFF-ZZZ.1
Additional information on the analysis of the target compound is available via Chemotion repository: https://dx.doi.org//RURBSASDZIORPD-UHFFFAOYSA-N.2

_N_-(2-Morpholinoethyl)pyrido[2',1':2,3]imidazo[4,5-c]isoquinolin-5-amine, 9e



GBB-product **4** (185 mg, 0.54 mmol, 1.00 equiv), 4-(2-isocyanoehtyl)morpholine (113.0 mg, 0.11 mL, 0.81 mmol, 1.5 equiv), potassium acetate (158.2 mg, 1.61 mmol, 3.00 equiv), Pd- Peppsi (18.3 mg, 0.03 mmol, 0.05 equiv) and XPhos (25.6 mg, 0.05 mmol, 0.10 equiv) were reacted in 3 mL DMF for 18 h at 120 °C. After purification *via* column chromatography (SiO_2, CH/EtOAc/NEt_3 20:1:0.05,to 0:1:0.05) insertion product **9e** was obtained as a yellow solid (57.0 mg, 0.16 mmol, 31%).

R_f (SiO_2, EtOAc) = 0.09.

^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm] = 8.65 (d, *J* = 8.1 Hz, 1H, CH_{Ar}), 8.59 (d, *J* = 6.8 Hz, 1H, CH_{Ar}), 7.95 (d, *J* = 8.3 Hz, 1H, CH_{Ar}), 7.80 (t, *J* = 7.5 Hz, 1H, CH_{Ar}), 7.69 (dt, *J* = 9.2 Hz, 1H, CH_{Ar}), 7.58 (ddd, *J* = 8.0, 7.0, 1.4 Hz, 1H, CH_{Ar}), 7.28-7.25 (m, 1H, CH_{Ar}), 6.86 (t, *J* = 6.7 Hz, 1H, CH_{Ar}), 6.24 (t, *J* = 4.7, 1H, N*H*), 3.79 (dt, *J* = 9.1, 5.0 Hz, 6H, CH_2), 2.81 (t, *J* = 6.0 Hz, 2H, CH_2), 2.59 (t, *J* = 4.4Hz, 4H, CH_2). Spectrum contains signals of H-grease and *N*-ethylacetamide.

^{13}C NMR (126 MHz, $CDCl_3$) δ [ppm] = 152.2 (C_q), 144.0 (C_q), 134.7 (C_q), 131.4 (C_q), 130.5 (CH_{Ar}), 125.8 (CH_{Ar}), 125.8 (CH_{Ar}), 123.2 (CH_{Ar}), 123.2 (CH_{Ar}), 123.0 (CH_{Ar}), 123.0 (CH_{Ar}), 119.1 (CH_{Ar}), 117.9 (CH_{Ar}), 111.9 (CH_{Ar}), 67.2 (2C, CH_2), 57.0 (CH_2), 53.5 (CH_2), 38,1 (2C, CH_2).

IR (ATR) $\tilde{\upsilon}$ [cm^{-1}] = 3271 (m), 3075 (w), 2952 (m), 2942 (w), 2932 (w), 2890 (w), 2868 (w), 2851 (m), 2812 (m), 2765 (w), 1655 (m), 1632 (s), 1625 (s), 1582 (vs), 1548 (vs), 1524 (vs), 1507 (vs), 1445 (s), 1421 (vs), 1377 (vs), 1350 (vs), 1306 (vs), 1258 (vs), 1217 (s), 1170 (m), 1145 (s), 1116 (vs), 1068 (s), 1034 (s), 1007 (s), 950 (m), 929

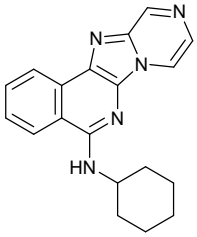
(s), 914 (s), 887 (s), 866 (s), 824 (m), 805 (m), 773 (vs), 744 (vs), 732 (vs), 711 (s), 670 (s), 636 (vs), 628 (vs), 613 (s), 591 (s), 568 (s), 547 (s), 521 (vs), 473 (s), 438 (s), 421 (s), 402 (m), 390 (s), 382 (s).

FAB-MS *m/z* (%): 349 (27), 348 $[M + H]^+$ (100), 347 (59), 346 (18), 262 (8), 261 (38), 260 (9), 259 (14), 248 (10), 247 (31), 246 (8), 235 (15), 234 (42), 233 (10), 219 (11), 149 (10), 136 (9), 118 (8), 114 (16), 100 (66), 91 (11), 90 (5), 89 (6).

HRMS-FAB (*m/z*): $[M + H]^+$ calcd. for $C_{20}H_{22}N_5O_1$: 348.1817; found, 348.1819.

Additional information on the chemical synthesis is available via Chemotion repository: https://dx.doi.org//reaction/SA-FUHFF-UHFFFADPSC-NYRZJQHSBU-UHFFFADPSC-NUHFF-NUHFF-NUHFF-ZZZ.1
Additional information on the analysis of the target compound is available via Chemotion repository: https://dx.doi.org//NYRZJQHSBUCBRV-UHFFFAOYSA-N.2

_N_-(Cyclohexylpyrazino[2',1':2,3]imidazo[4,5-c]isoquinolin-5-amine, 10a



GBB-product **5** (200 mg, 0.58 mmol, 1.00 equiv), cyclohexyl isocyanide (95.2 mg, 0.11 mL, 0.87 mmol, 1.50 equiv), potassium acetate (171 mg, 1.74 mmol, 3.00 equiv), Pd-Peppsi-iPr (19.8 mg, 0.03 mmol, 0.05 equiv) and XPhos (27.7 mg, 0.06 mmol, 0.10 equiv) were reacted in 3 mL DMF for 18 h at 120 °C. After purification *via* column chromatography (SiO_2, CH/EtOAc/NEt_3 20:1:0.05 to 2:1:0.05) insertion product **10a** was obtained as a yellow solid (124 mg, 0.39 mmol, 67%).

R_f (SiO_2, CH/EtOAc 2:1) = 0.22.

^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm] = 9.16 (s, 1H, CH_{Ar}), 8.64 (d, *J* = 8.0, 1H, CH_{Ar}), 8.43 (d, *J* = 4.5 Hz, 1H, CH_{Ar}), 7.91-7.88 (m, 2H, CH_{Ar}), 7.82 (t, *J* = 7.56 Hz, 1H, CH_{Ar}), 7.60 (t, *J* = 7.7 Hz, 1H, CH_{Ar}), 5.50 (d, *J* = 7.3 Hz, 1H, N*H*), 4.35-4.28 (m, 1H, C*H*), 2.25 (dd, *J* = 12.4, 4.4 Hz, 2H, CH_2), 1.85 (dt, *J* = 13.5, 4.0 Hz, 2H, CH_2), 1.58-1.50 (m, 2H, CH_2), 1.40-1.23 (m, 4H, CH_2).

^{13}C NMR (126 MHz, $CDCl_3$) δ [ppm] = 152.6 (C_q), 144.4 (C_q), 138.3 (C_q), 134.6 (C_q), 131.5 (C_q), 130.9 (CH_{Ar}), 127.8 (C_q), 127.4 (CH_{Ar}), 126.8 (CH_{Ar}), 123.3 (CH_{Ar}), 122.8 (CH_{Ar}), 120.0 (C_q), 115.9 (CH_{Ar}), 50.3 (*C*H), 33.2 (CH_2), 26.0 (CH_2), 25.3 (CH_2).

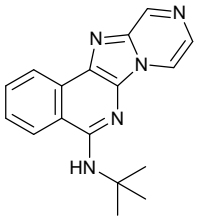
IR (ATR) $\tilde{\upsilon}$ [cm^{-1}] = 3233 (w), 2920 (w), 2851 (w), 1655 (w), 1573 (m), 1543 (m), 1493 (m), 1449 (w), 1373 (w), 1327 (w), 1293 (w), 1253 (m), 1150 (w), 1067 (w), 1030 (w), 1005 (w), 938 (w), 890 (w), 763 (w), 711 (w), 664 (w), 646 (w), 597 (w), 567 (w), 522 (w), 417 (w).

FAB-MS *m/z* (%): 318 $[M + H]^+$ (100), 317 $[M]^+$ (56), 235 $[M - C_6H_{11} + H]^+$ (24).

HRMS-FAB (*m/z*): $[M + H]^+$ calcd. for $C_{19}H_{20}N_5$, 318.1719; found, 318.1717.

Additional information on the chemical synthesis is available via Chemotion repository: https://dx.doi.org//reaction/SA-FUHFF-UHFFFADPSC-WEKJKTOCUO-UHFFFADPSC-NUHFF-NUHFF-NUHFF-ZZZ
Additional information on the analysis of the target compound is available via Chemotion repository: https://dx.doi.org//WEKJKTOCUOAZQD-UHFFFAOYSA-N.1

_N_-(_tert_-Butyl)pyrazino[2',1':2,3]imidazo[4,5-c]isoquinolin-5-amine, 10b



GBB-product **5** (120 mg, 0.35 mmol, 1.00 equiv), tert-butyl isocyanide (43.3 mg, 0.06 mL, 0.52 mmol, 1.5 equiv), potassium acetate (102 mg, 1.04 mmol, 3.00 equiv), Pd-Peppsi-iPr (11.8 mg, 0.02 mmol, 0.05 equiv) and XPhos (16.6 mg, 0.03 mmol, 0.10 equiv) were reacted in 3 mL DMF for 18 h at 120 °C. After purification *via* column chromatography (SiO_2, CH/EtOAc/NEt_3 20:1:0.05 to 2:1:0.05) insertion product **10b** was obtained as a yellow solid (20 mg, 0.07 mmol, 20%).

R_f (SiO_2, CH/EtOAc 2:1) = 0.18.

^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm] = 9.18 (d, J = 1.5 Hz, 1H, CH_{Ar}), 8.67 (d, J = 7.9 Hz, 1H, CH_{Ar}), 8.43 (dd, J = 4.6, 1.6 Hz, 1H, CH_{Ar}), 7.92 (d, J = 4.6 Hz 1H, CH_{Ar}), 7.86-7.81 (m, 2H, CH_{Ar}), 7.63-7.55 (m, 1H, CH_{Ar}), 5.51 (s, 1H, N*H*), 1,7 (s, 9H, CH_3).

^{13}C NMR (126 MHz, $CDCl_3$) δ [ppm] = 152.5 (C_q), 144.5 (C_q), 138.4 (C_q), 134.2 (C_q), 131.7 (C_q), 130.8 (CH_{Ar}), 127.9 (C_q), 127.2 (CH_{Ar}), 126.9 (CH_{Ar}), 123.4 (CH_{Ar}), 122.9z (CH_{Ar}), 120.5 (C_q), 115.9 (C_q), 52.6 (C_q), 29.1 (3C, CH_3).

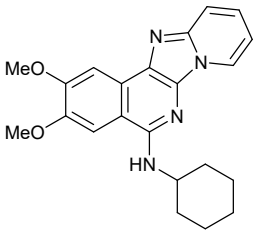
IR (ATR) $\tilde{\upsilon}$ [cm^{-1}] = 3418 (w), 2965 (m), 2918 (w), 2868 (w), 1728 (w), 1613 (w), 1608 (vw), 1572 (vs), 1538 (vs), 1524 (s), 1496 (s), 1487 (s), 1476 (vs), 1451 (s), 1435 (m), 1421 (m), 1383 (m), 1370 (s), 1356 (m), 1346 (m), 1322 (m), 1299 (s), 1286 (m), 1269 (s), 1256 (vs), 1213 (vs), 1179 (m), 1171 (m), 1152 (s), 1128 (m), 1102 (m), 1094 (m), 1079 (m), 1030 (m), 1009 (m), 929 (m), 892 (w), 867 (w), 798 (m), 765 (vs), 738 (m), 711 (s), 698 (m), 670 (vs), 656 (s), 633 (vs), 595 (vs), 561 (m), 523 (vs), 480 (m), 442 (s), 419 (m), 412 (m), 390 (s).

FAB-MS *m/z* (%): 367 (13), 366 (12), 293 (26), 292 $[M + H]^+$ (100), 291 (56), 259 (15), 237 (17), 236 (52), 235 (43), 207 (12), 189 (11), 177 (12), 155 (11), 154 (27), 147 (29), 145 (11), 138 (11), 137 (20), 136 (48), 135 (11), 133 (12), 131 (14), 129 (12), 128 (11), 123 (13), 121 (15), 120 (12), 119 (13), 117 (14), 115 (14), 109 (19), 107 (28), 106 (14), 105 (25), 97 (16), 95 (29), 93 (16), 91 (46), 90 (26), 89 (21).

HRMS-FAB (*m/z*): $[M + H]^+$ calcd. for $C_{18}H_{19}N_4$, 292.1557; found, 292.1559.

Additional information on the chemical synthesis is available via Chemotion repository: https://dx.doi.org//reaction/SA-FUHFF-UHFFFADPSC-UDIATBZHGY-UHFFFADPSC-NUHFF-NUHFF-NUHFF-ZZZ
Additional information on the analysis of the target compound is available via Chemotion repository: https://dx.doi.org//UDIATBZHGYLNCJ-UHFFFAOYSA-N

***N*-Cyclohexyl-2,3-dimethoxypyrido[2',1':2,3]imidazo[4,5-c]isochinolin-5-amine, 11a**



GBB-product **6** (200 mg, 495 µmol, 1.00 equiv.), cyclohexyl isocyanide (81 mg, 92 µL, 741 µmol, 1.50 equiv.), potassium acetate (146 mg, 1.48 mmol, 3.00 equiv.), PEPPSI-iPr (16.9 mg, 24.7 µmol, 0.05 equiv.) and XPhos (23.6 mg, 49.5 µmol, 0.10 equiv.) were reacted in 2 mL DMF for 16 h at 120 °C. After purification *via* flash-chromatography (SiO2, CH/EtOAc/NEt3 6:1:0.01 to 1:2:0.04), insertion product **11a** was obtained as a yellow solid (113 mg, 300 µmol, 61% yield).

***R*$_f$** (SiO_2, CH/EtOAc 1:2) = 0.08.

^{1}H-NMR (500 MHz, $CDCl_3$) δ [ppm] =8.60 (d, *J* = 6.8 Hz, 1H, CH_{Ar}), 7.99 (s, 1H, CH_{Ar}), 7.69 (d, *J* = 9.1 Hz, 1H, CH_{Ar}), 7.27 (t, *J* = 7.2 Hz, 1H, CH_{Ar}), 7.19 (s, 1H, CH_{Ar}), 6.87 (td, *J* = 6.8, 1.1 Hz, 1H, CH_{Ar}), 5.14 (d, *J* = 6.3 Hz, 1H, N*H*), 4.38 – 4.25 (m, 1H, C*H*), 4.08 (s, 3H, OCH_3), 4.01 (s, 3H, OCH_3), 2.28 (dd, *J* = 12.5, 3.9 Hz, 2H, CH_2), 1.84 (dt, *J* = 13.6, 3.8 Hz, 2H, CH_2), 1.73 (dt, *J* = 12.9, 3.7 Hz, 1H, CH_2), 1.59 – 1.45 (m, 2H, CH_2), 1.43 – 1.26 (m, 3H, CH_2). Spectrum contains signals of tautomers.

^{13}C-NMR (126 MHz, $CDCl_3$) δ [ppm] = 152.6 (C_q), 150.6 (C_q), 148.7 (C_q), 143.3 (C_q), 134.1 (C_q), 126.8 (C_q), 126.2 (CH_{Ar}), 124.8 (C_q), 123.4 (CH_{Ar}), 117.1 (CH_{Ar}), 113.2 (C_q), 111.0 (CH_{Ar}), 103.5 (CH_{Ar}), 103.0 (CH_{Ar}), 56.5 (CH_3), 56.4 (CH_3), 50.5 (CH), 33.5 (2C, CH_2), 26.2 (CH_2), 25.5 (2C, CH_2).

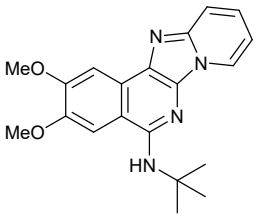
IR (ATR) $\tilde{\upsilon}$ [cm^{-1}] = 3223 (w), 2999 (w), 2925 (m), 2850 (w), 1731 (w), 1621 (w), 1589 (m), 1568 (m), 1547 (s), 1520 (m), 1503 (s), 1487 (vs), 1459 (m), 1432 (vs), 1385 (s), 1370 (m), 1351 (s), 1322 (m), 1290 (m), 1252 (vs), 1215 (vs), 1203 (vs), 1179 (vs), 1146 (s), 1112 (m), 1067 (s), 1047 (m), 1033 (m), 1004 (m), 993 (m), 938 (w), 929 (w), 888 (w), 864 (m), 849 (m), 824 (s), 803 (w), 779 (m), 748 (vs), 735 (s), 652 (m), 626 (s), 589 (m), 572 (m), 557 (m), 534 (w), 513 (w), 466 (w), 452 (w), 414 (m), 388 (w), 378 (w).

FAB-MS *m/z* (%):378 (19), 377 (81), 376 $[M]^+$ (100), 375 (13), 294 (8), 154 (14), 137 (9), 136 (11).

HRMS-FAB (*m/z*): [M + H]+ calcd. for $C_{22}H_{24}O_2N_4$, 376.1894; found, 376.1893.

Additional information on the chemical synthesis is available via Chemotion repository: https://dx.doi.org//reaction/SA-FUHFF-UHFFFADPSC-LIGYTKHHUT-UHFFFADPSC-NUHFF-NUHFF-NUHFF-ZZZ.1
Additional information on the analysis of the target compound is available via Chemotion repository: https://dx.doi.org//LIGYTKHHUTXHBA-UHFFFAOYSA-N.2

***N*-(*tert.*-Butyl)-2,3-dimethoxypyrido[2',1':2,3]imidazo[4,5-c]isoquinoline-5-amine, 11b**



GBB-product **6** (100 mg, 0.25 mmol, 1.00 equiv.), *tert*.-butyl isocyanide (31 mg, 0.04 mL, 0.37 mmol, 1.50 equiv.), potassium acetate (73 mg, 0.74 mmol, 3.00 equiv.), $Pd(dba)_2$ (7.1 mg, 0.012 mmol, 0.05 equiv.) and XPhos (12 mg, 0.025 mmol, 0.10 equiv.) were reacted in 2 mL DMF for 18 h at 120 °C. After purification *via* preparative TLC (SiO_2, CH/EtOAc/NEt_3 6:1:0.04, then 1:1:0.04) insertion product **11b** was obtained as a yellow solid (47 mg, 0.13 mmol, 54%).

R_f (SiO_2, CH/EtOAc 1:1) = 0.45.

^{1}H-NMR (400 MHz, $CDCl_3$) δ [ppm] = 8.56 (d, J = 6.8 Hz, 1H, CH_{Ar}), 7.97 (d, J = 6.7 Hz, 1H, CH_{Ar}), 7.65 (dd, J = 9.1, 1.1 Hz, 1H, CH_{Ar}), 7.11 (s, 1H, CH_{Ar}), 6.83 (td, J = 6.7, 1.1 Hz, 1H, CH_{Ar}), 5.04 (s, 1H, NH), 4.07 (s, 3H, OCH_3), 4.01 (s, 3H, OCH_3), 1.67 (s, 9H, CH_3). Spectrum contains signals of tautomers and DMF.

^{13}C-NMR (101 MHz, $CDCl_3$) δ [ppm] = 152.4 (C_q), 150.3 (C_q), 148.6 (C_q), 143.6 (C_q), 133.8 (C_q), 127.0 (C_q), 125.9 (CH_{Ar}), 125.0 (C_q), 123.2 (CH_{Ar}), 117.3 (CH_{Ar}), 113.6 (C_q), 110.7 (CH_{Ar}), 103.6 (CH_{Ar}), 102.9 (CH_{Ar}), 56.5 (CH_3), 56.3 (CH_3), 52.3 (C_q), 29.3 (3C, CH_3).

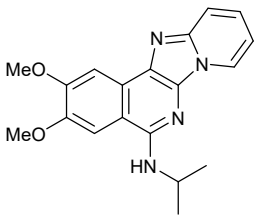
IR (ATR) $\tilde{\upsilon}$ [cm^{-1}] = 2961 (vw), 2255 (w), 2172 (w), 1624 (w), 1590 (w), 1574 (w), 1538 (w), 1479 (w), 1430 (w), 1390 (w), 1346 (w), 1310 (w), 1290 (w), 1251 (w), 1201 (m), 1180 (w), 1090 (w), 1071 (w), 1035 (w), 1005 (w), 993 (w), 938 (w), 913 (w), 854 (w), 824 (w), 787 (w), 745 (w), 723 (m), 662 (w).

FAB-MS *m/z* (%): 338 (17), 337 (81), 336 $[M]^+$ (100).

HRMS-FAB (*m/z*): $[M]^+$ calcd. for $C_{19}H_{20}O_2N_4$, 336.1586; found, 336.1585.

Additional information on the chemical synthesis is available via Chemotion repository: https://dx.doi.org//reaction/SA-FUHFF-UHFFFADPSC-RGRCDEZDHR-UHFFFADPSC-NUHFF-NUHFF-NUHFF-ZZZ.1
Additional information on the analysis of the target compound is available via Chemotion repository: https://dx.doi.org//RGRCDEZDHRBRJV-UHFFFAOYSA-N.2

***N*-Isopropyl-2,3-dimethoxypyrido[2',1':2,3]imidazo[4,5-c]isoquinolin-5-amine, 11c**



GBB-product **6** (100 mg, 0.25 mmol, 1.00 equiv.), isopropyl isocyanide (26 mg, 0.04 mL, 0.37 mmol, 1.50 equiv.), potassium acetate (73 mg, 0.74 mmol, 3.00 equiv.), $Pd(dba)_2$ (7.1 mg, 0.012 mmol, 0.05 equiv.) and XPhos (12 mg, 0.025 mmol, 0.10 equiv.) were reacted in 2 mL DMF for 18 h at 120 °C. After purification *via* preparative TLC (SiO_2, CH/EtOAc/NEt_3 6:1:0.04, then 1:1:0.04) insertion product **11c** was obtained as a yellow solid (32 mg, 0.10 mmol, 39%).

***R*$_f$** (SiO_2, CH/EtOAc 1:1) = 0.45.

^{1}H-NMR (400 MHz, $CDCl_3$) δ [ppm] = 8.63 – 8.56 (m, 1H, C*H*$_{Ar}$), 8.02 – 7.94 (m, 1H, C*H*$_{Ar}$), 7.75 – 7.59 (m, 1H, C*H*$_{Ar}$), 7.23 (d, *J* = 23.5 Hz, 2H, C*H*$_{Ar}$), 6.88 – 6.82 (m, 1H, C*H*$_{Ar}$), 5.10 (s, 1H, N*H*), 4.60 (d, *J* = 6.8 Hz, 1H, C*H*), 4.07 (s, 3H, C*H*$_3$), 4.01 (s, 3H, C*H*$_3$), 1.48 – 1.34 (m, 6H, C*H*$_3$). Spectrum contains signals of tautomers and DMF.

^{13}C-NMR (101 MHz, $CDCl_3$) δ [ppm] = 152.6 (C_q), 150.6 (C_q), 148.7 (C_q), 143.6 (C_q), 134.2 (C_q), 126.9 (C_q), 126.0 (CH_{Ar}), 125.2 (C^q), 123.3 (CH_{Ar}), 117.3 (CH_{Ar}), 113.2 (C_q), 110.8 (CH_{Ar}), 103.5 (CH_{Ar}), 103.0 (CH_{Ar}), 56.5 (CH_3), 56.4 (CH_3), 43.4 (CH), 23.1 (2C, CH_3).

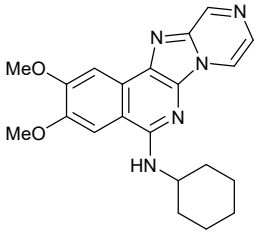
IR (ATR) $\tilde{\upsilon}$ [cm^{-1}] = 3419 (w), 3235 (vw), 2965 (w), 2255 (vw), 1626 (w), 1588 (w), 1573 (w), 1546 (w), 1487 (m), 1433 (m), 1387 (w), 1349 (w), 1321 (w), 1293 (w), 1250 (m), 1204 (m), 1181 (m), 1087 (w), 1070 (w), 1034 (w), 1005 (w), 915 (w), 850 (w), 824 (w), 783 (w), 728 (m), 656 (w), 628 (m), 571 (w).

FAB-MS *m/z* (%): 351 $[M + H]^+$ (84), 350 $[M]^+$ (100), 294 $[M – tBu + H]^+$ (15), 293 $[M – tBu]^+$ (3).

HRMS-FAB (*m/z*): $[M]^+$ calcd. for $C_{19}H_{20}O_2N_4$, 336.1586; found, 336.1585.

Additional information on the chemical synthesis is available via Chemotion repository: https://dx.doi.org//reaction/SA-FUHFF-UHFFFADPSC-VJUXHPAAXF-UHFFFADPSC-NUHFF-NUHFF-NUHFF-ZZZ
Additional information on the analysis of the target compound is available via Chemotion repository: https://dx.doi.org//VJUXHPAAXFEYKZ-UHFFFAOYSA-N.1

***N*- Cyclohexyl -2,3-dimethoxypyrazino[2',1':2,3]imidazo[4,5-c]isoquinolin-5-amine, 12a**



GBB-product **7** (200 mg, 0.58 mmol, 1.00 equiv), *tert*-butyl isocyanide (61.5 mg, 0.08 mL, 0.74 mmol, 1.5 equiv), potassium acetate (145 mg, 1.48 mmol, 3.00 equiv), Pd-Peppsi (16.8 mg, 0.02 mmol, 0.05 equiv) and XPhos (23.5 mg, 0.05 mmol, 0.10 equiv) were reacted in 3 mL DMF for 18 h at 120 °C. After purification *via* column chromatography (SiO_2, CH/EtOAc/NEt_3 20:1:0.05 to 1:2:0.05) insertion product **12a** was obtained as a yellow solid (77 mg, 0.20 mmol, 41%).

***R*$_f$** (SiO_2, CH/EtOAc 1:2) = 0.21.

^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm] = 9.11 (d, *J* = 1.6 Hz, 1H, C*H*$_{Ar}$), 8.41 (dd, *J* = 4.6, 1.6 Hz, 1H, C*H*$_{Ar}$), 7.93 (s, 1H, C*H*$_{Ar}$), 7.87 (d, *J* = 4.6 Hz, 1H, C*H*$_{Ar}$), 7.20 (s, 1H, C*H*$_{Ar}$), 5.41 (d, *J* = 7.2 Hz, 1H, N*H*), 4.29 (dtd, *J* = 10.7, 6.9, 3.6 Hz, 1H), 4.05 (s, 3H, OC*H*$_3$), 3.98 (s, 3H, OC*H*$_3$),), 2.24 (dd, *J* = 12.4, 3.9 Hz, 2H, C*H*$_2$), 1.86 – 1.80 (m, 2H, C*H*$_2$), 1.71 (dt, *J* = 13.2, 3.7 Hz, 1H, C*H*$_2$), 1.60 – 1.43 (m, 2H, C*H*$_2$), 1.42 – 1.25 (m, 3H, C*H*$_2$). Spectrum contains signals of tautomers and *N*-ethylacetamide.

^{13}C NMR (101 MHz, $CDCl_3$) δ [ppm] = 152.7 (C_q), 151.9 (C_q), 149.4 (C_q), 143.9 (C_q), 138.1 (C_q), 134.0 (C_q), 127.6 (CH_{Ar}), 127.4 (CH_{Ar}), 127.0 (CH_{Ar}), 115.9 (CH_{Ar}), 114.1 (CH_{Ar}), 103.8 (C_q), 103.1 (C_q), 56.5 (CH_3), 56.3 (CH_3), 50.5 (CH), 33.3 (2C, CH_2), 26.0 (CH_2), 25.4 (2C, CH_2).

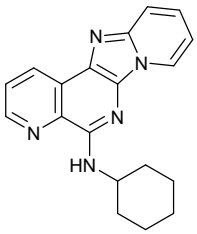
IR (ATR) $\tilde{u}$ [cm^{-1}] = 3408 (w), 3312 (w), 2924 (m), 2850 (m), 1615 (w), 1574 (s), 1540 (s), 1486 (vs), 1432 (vs), 1381 (s), 1346 (s), 1282 (s), 1248 (vs), 1205 (vs), 1180 (vs), 1069 (s), 1027 (m), 1006 (s), 999 (s), 856 (s), 826 (m), 786 (vs), 626 (vs), 599 (s), 412 (s), 377 (s).

FAB-MS *m/z* (%): 379 $[M + 2H]^+$ (29), 378 $[M + H]^+$ (100), 377 $[M]^+$ (56), 376 $[M – H]^+$ (11), 362 (7), 296 (15), 295 (20), 280 (12), 133 (11).

HRMS-FAB (*m/z*): $[M + H]^+$ calcd. for $C_{21}H_{24}O_2N_5$, 378.1925; found, 378.1923.

Additional information on the chemical synthesis is available via Chemotion repository: https://dx.doi.org//reaction/SA-FUHFF-UHFFFADPSC-OQALJCKHBA-UHFFFADPSC-NUHFF-NUHFF-NUHFF-ZZZ.1
Additional information on the analysis of the target compound is available via Chemotion repository: https://dx.doi.org//OQALJCKHBAHWFS-UHFFFAOYSA-N.2

_N_-Cyclohexylpyrido[1',2':1,2]imidazo[4,5-f][1,7]naphthyridin-5-amine, 13a



GBB-product **8** (75 mg, 0.22 mmol, 1.00 equiv.), cyclohexyl isocyanide (36 mg, 0.05 mL, 0.33 mmol, 1.50 equiv.), potassium acetate(64 mg, 0.65 mmol, 3.00 equiv.), $Pd(dba)_2$ (6.2 mg, 0.011 mmol, 0.05 equiv.) and XPhos (10 mg, 0.02 mmol, 0.10 equiv.) were reacted in 2 mL DMF for 18 h at 120 °C. After purification *via* preparative TLC (SiO_2, CH/EtOAc/NEt_3 6:1:0.04, then 1:1:0.04) insertion product **13a** was obtained as a yellow solid (18 mg, 0.06 mmol, 39%).

R_f (SiO_2, CH/EtOAc 1:2) = 0.17.

^{1}H-NMR (400 MHz, $CDCl_3$) δ [ppm] = 8.84 (dd, *J* = 8.2, 1.9 Hz, 1H, CH_{Ar}), 8.76 (dd, *J* = 4.4, 1.7 Hz, 1H, CH_{Ar}), 8.60 (d, *J* = 6.9 Hz, 1H, CH_{Ar}), 7.68 – 7.62 (m, 1H, CH_{Ar}), 7.31 – 7.20 (m, 1H, CH_{Ar}), 7.06 (d, *J* = 8.1 Hz, 1H, CH_{Ar}), 6.85 (t, *J* = 6.7 Hz, 1H, CH_{Ar}), 5.49 (d, *J* = 60.5 Hz, 1H, N*H*), 4.24 (dtt, *J* = 10.0, 7.7, 4.0 Hz, 1H, C*H*), 2.38 – 2.13 (m, 2H, CH_2), 1.85 (dt, *J* = 12.4, 3.8 Hz, 2H, CH_2), 1.70 (ddq, *J* = 13.5, 8.4, 4.0 Hz, 2H, CH_2), 1.59 – 1.50 (m, 2H, CH_2), 1.50 – 1.41 (m, 2H, CH_2).

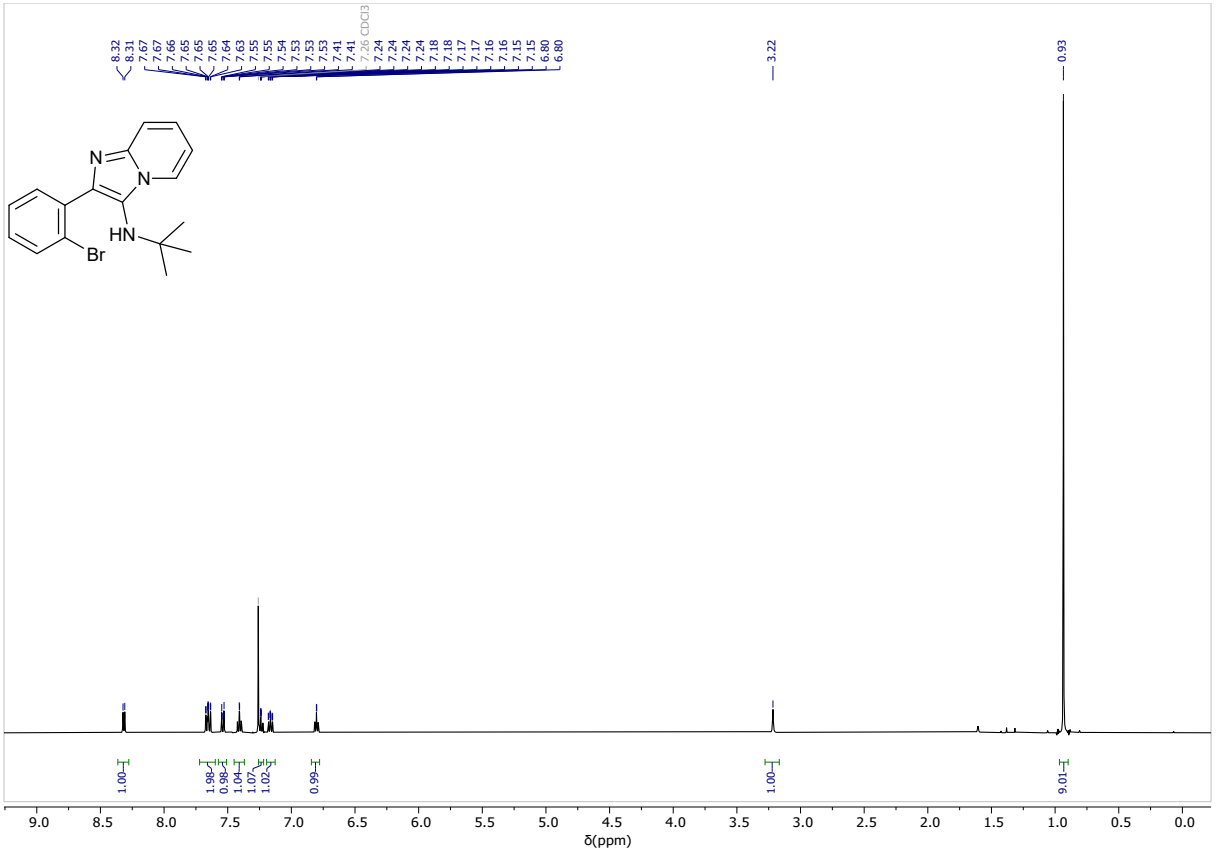
^{13}C-NMR (101 MHz, $CDCl_3$) δ [ppm] = 152.1 (C_q), 147.0 (CH_{Ar}), 144.1 (C_q), 135.3 (C_q), 135.2 (C_q), 130.7 (CH_{Ar}), 126.4 (C_q), 125.8 (CH_{Ar}), 125.3 (CH_{Ar}), 123.4 (CH_{Ar}), 123.4 (C_q), 117.7 (CH_{Ar}), 111.0 (CH_{Ar}), 49.6 (CH), 33.1 (2C, CH_2), 26.1 (2C, CH_2), 25.3 (CH_2).

IR (ATR) $\tilde{\upsilon}$ [cm^{-1}] = 3391 (w), 2923 (m), 2851 (m), 1655 (m), 1585 (m), 1520 (s), 1447 (m), 1398 (m), 1375 (m), 1347 (m), 1303 (w), 1252 (m), 1228 (m), 1151 (w), 1112 (w), 1075 (w), 918 (w), 890 (w), 815 (w), 797 (w), 734 (m), 668 (m), 644 (m), 424 (m), 409 (w).

FAB-MS *m/z* (%): 318 $[M + H]^+$ (100), 317 $[M]^+$ (98), 235 $[M - C_6H_{11} + H]^+$ (18).

HRMS-FAB (*m/z*): $[M + H]^+$ calcd. for $C_{19}H_{20}N_5$, 318.1719; found, 318.1720.

Additional information on the chemical synthesis is available via Chemotion repository: https://dx.doi.org//reaction/SA-FUHFF-UHFFFADPSC-HFAHLVSLTU-UHFFFADPSC-NUHFF-NUHFF-NUHFF-ZZZ.1
Additional information on the analysis of the target compound is available via Chemotion repository: https://dx.doi.org//HFAHLVSLTUNYSC-UHFFFAOYSA-N.2


8.32
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7.67
7.66
7.65
7.65
7.65
7.64
7.63
7.55
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7.53
7.53
7.41
7.41
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7.17
7.17
7.16
7.16
7.15
7.15
6.80
6.80
3.22
0.93
N
N
HN
Br
1.00
1.98
0.98
1.04
1.07
1.02
0.99
1.00
9.01
9.0
8.5
8.0
7.5
7.0
6.5
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5.0
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δ(ppm)

Figure 1 ***^{1}H-NMR-Spectrum of Compound 4.***

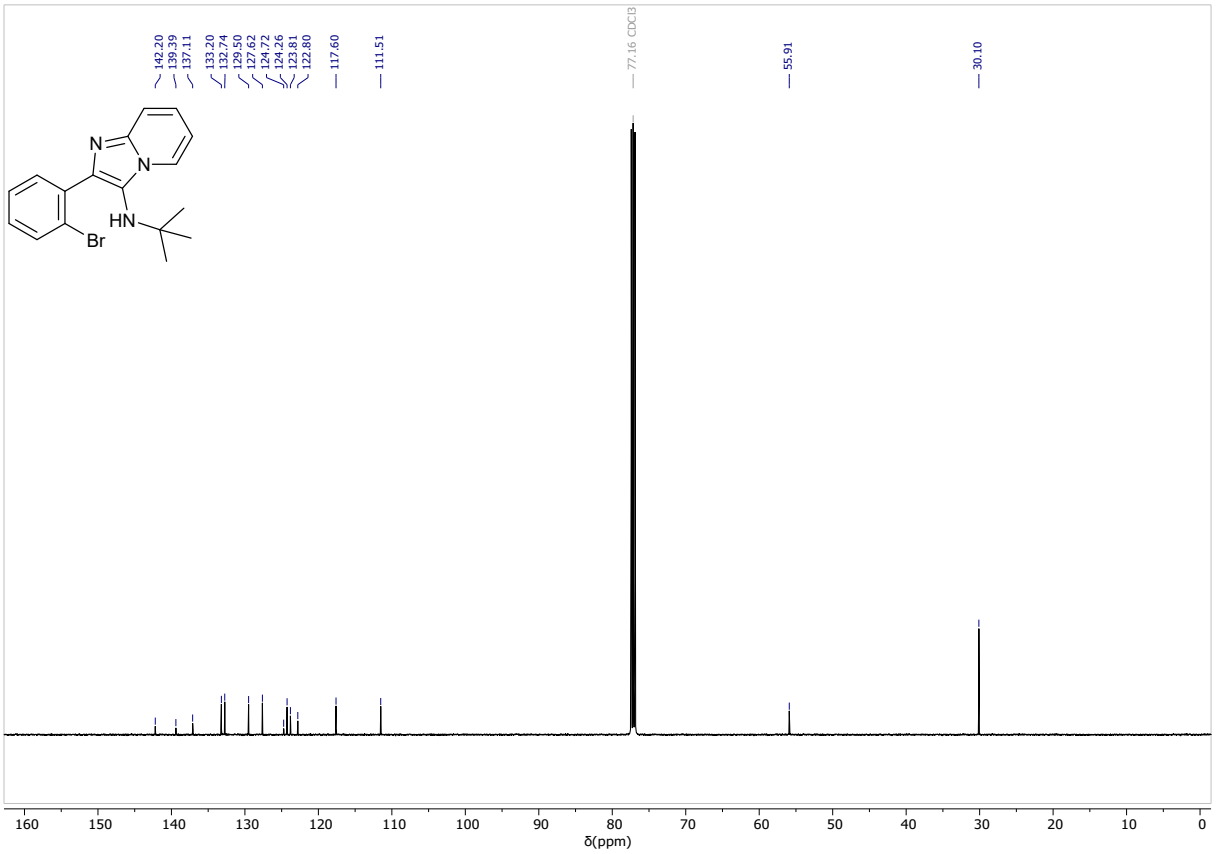


Figure 2 ***^{13}C-NMR-Spectrum of Compound 4.***

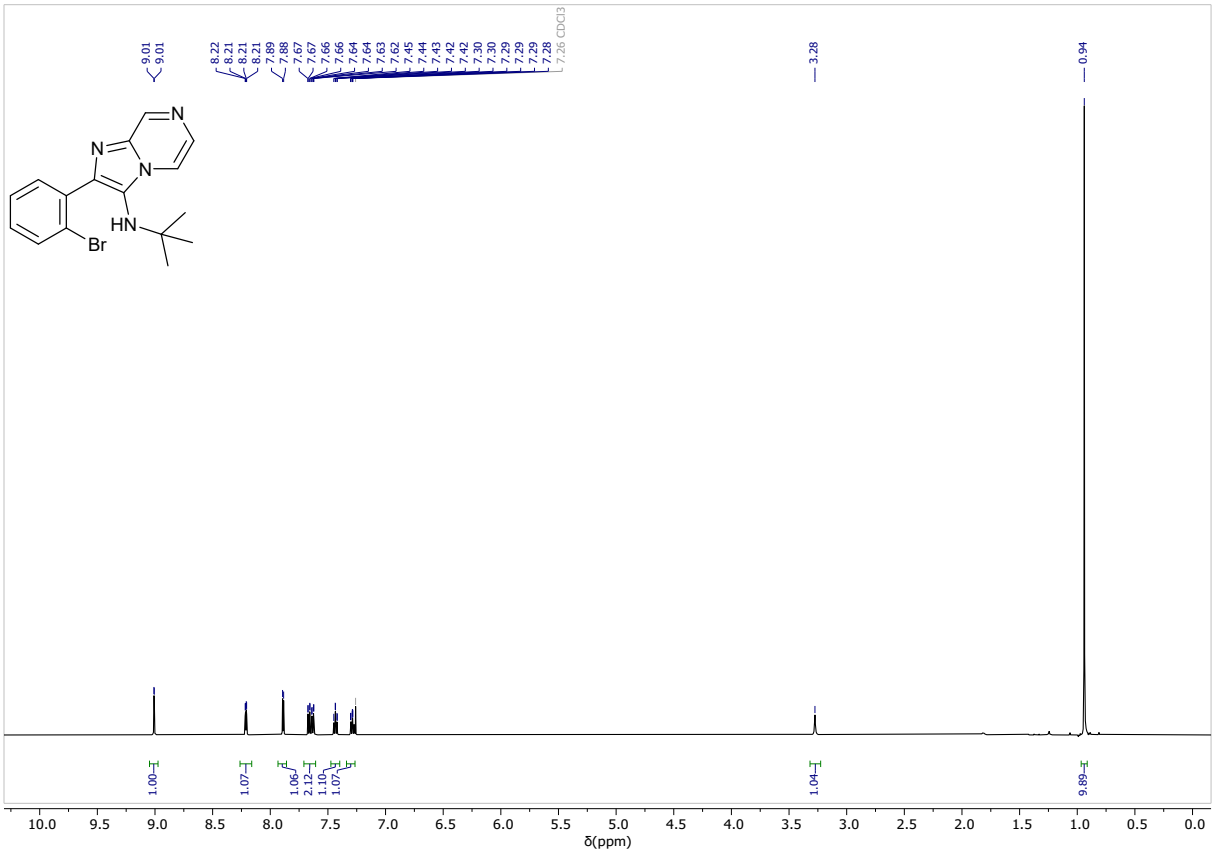


Figure 3 ***^{1}H-NMR-Spectrum of Compound 5.***

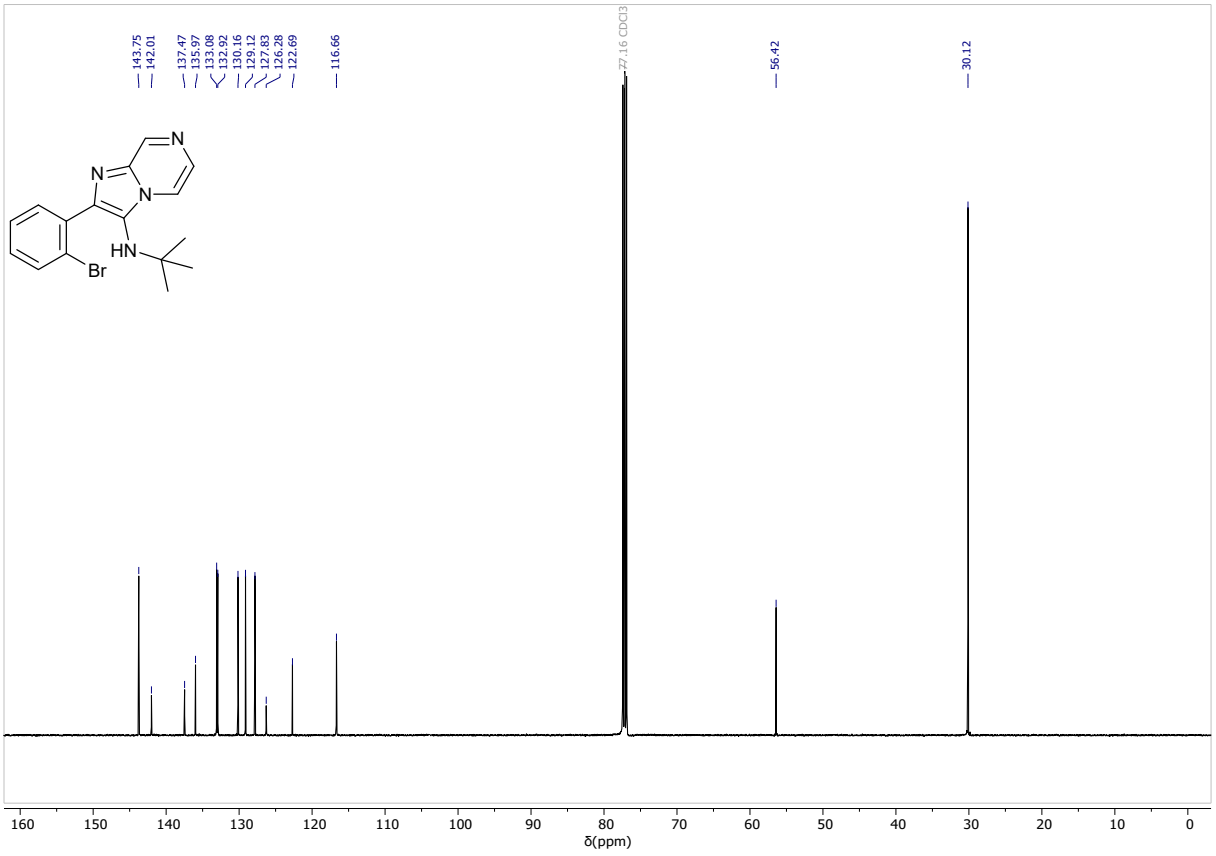


Figure 4 ***^{13}C-NMR-Spectrum of Compound 5.***

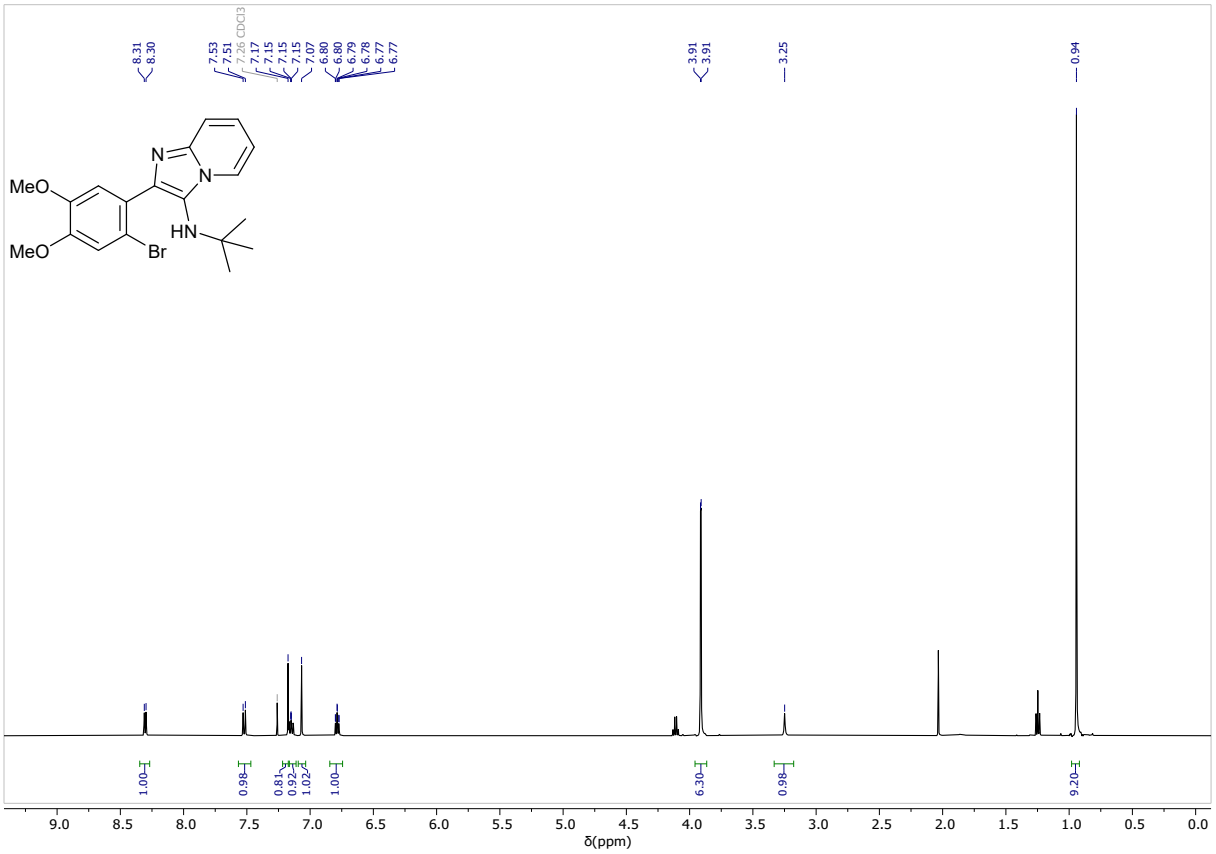


Figure 5 ***^{1}H-NMR-Spectrum of Compound 6.***

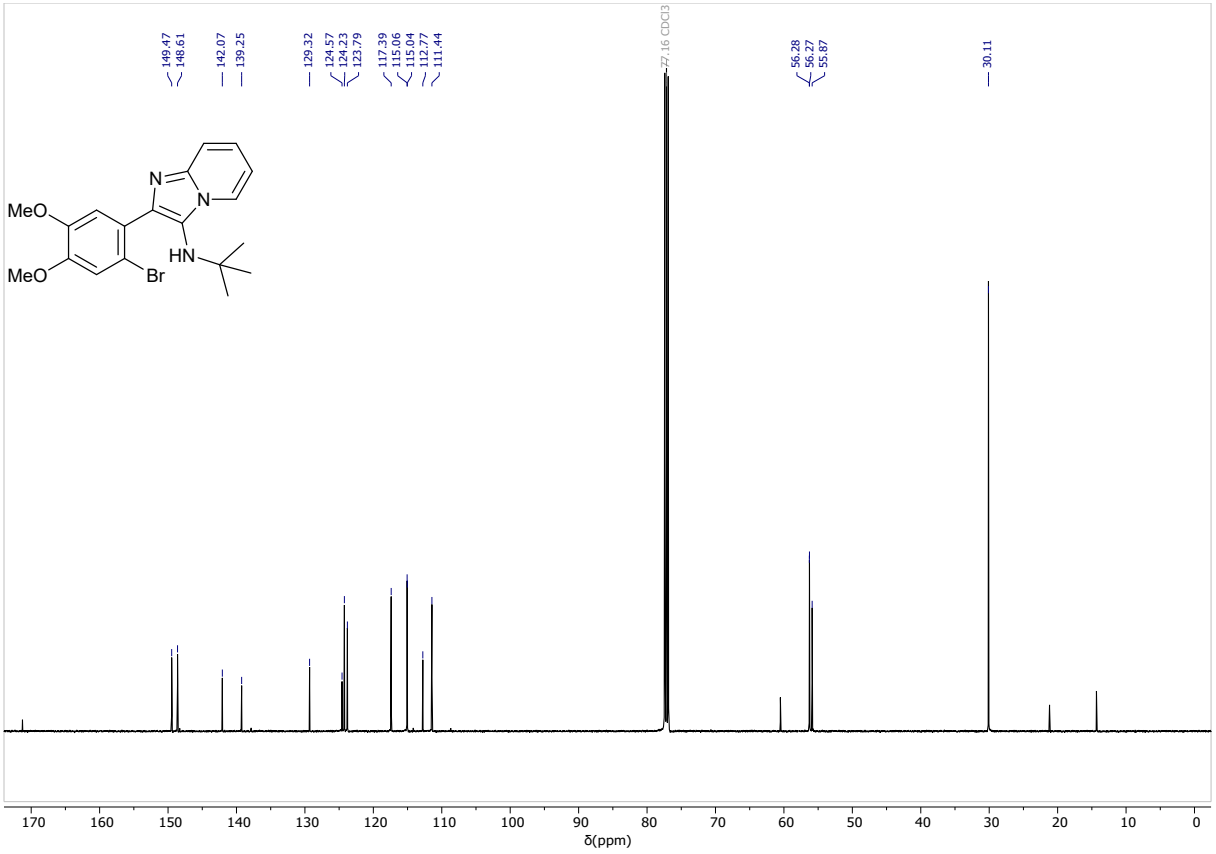


Figure 6 ***^{13}C-NMR-Spectrum of Compound 6.***

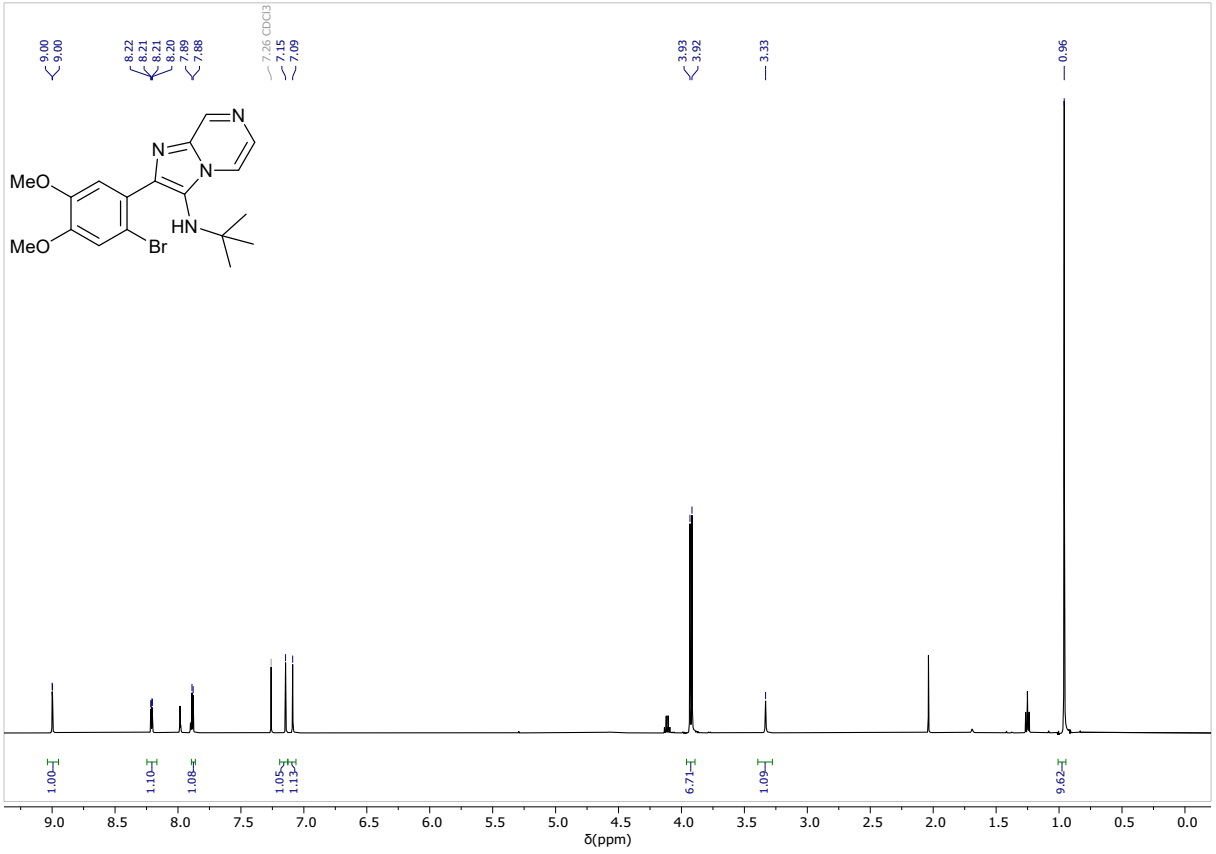


Figure 7 ***^{1}H-NMR-Spectrum of Compound 7.***

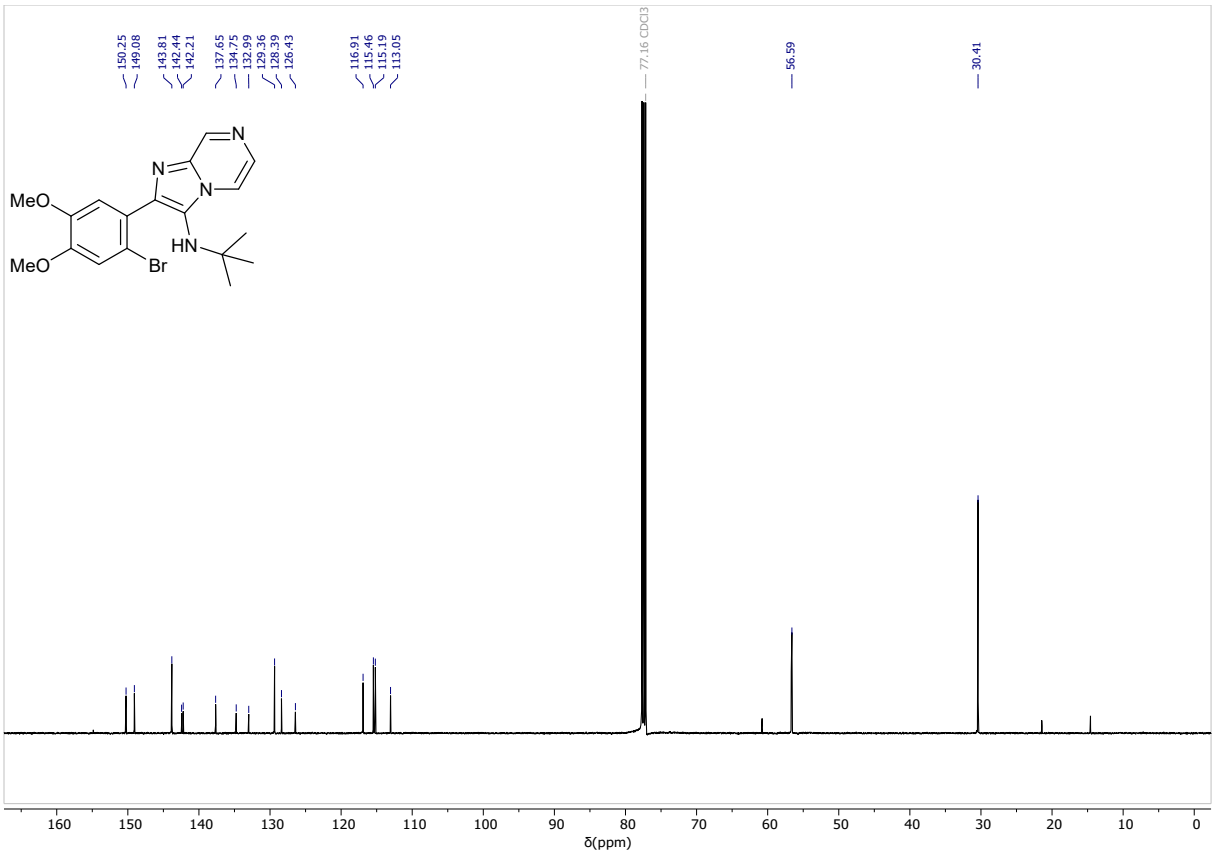


Figure 8 ***^{13}C-NMR-Spectrum of Compound 7.***

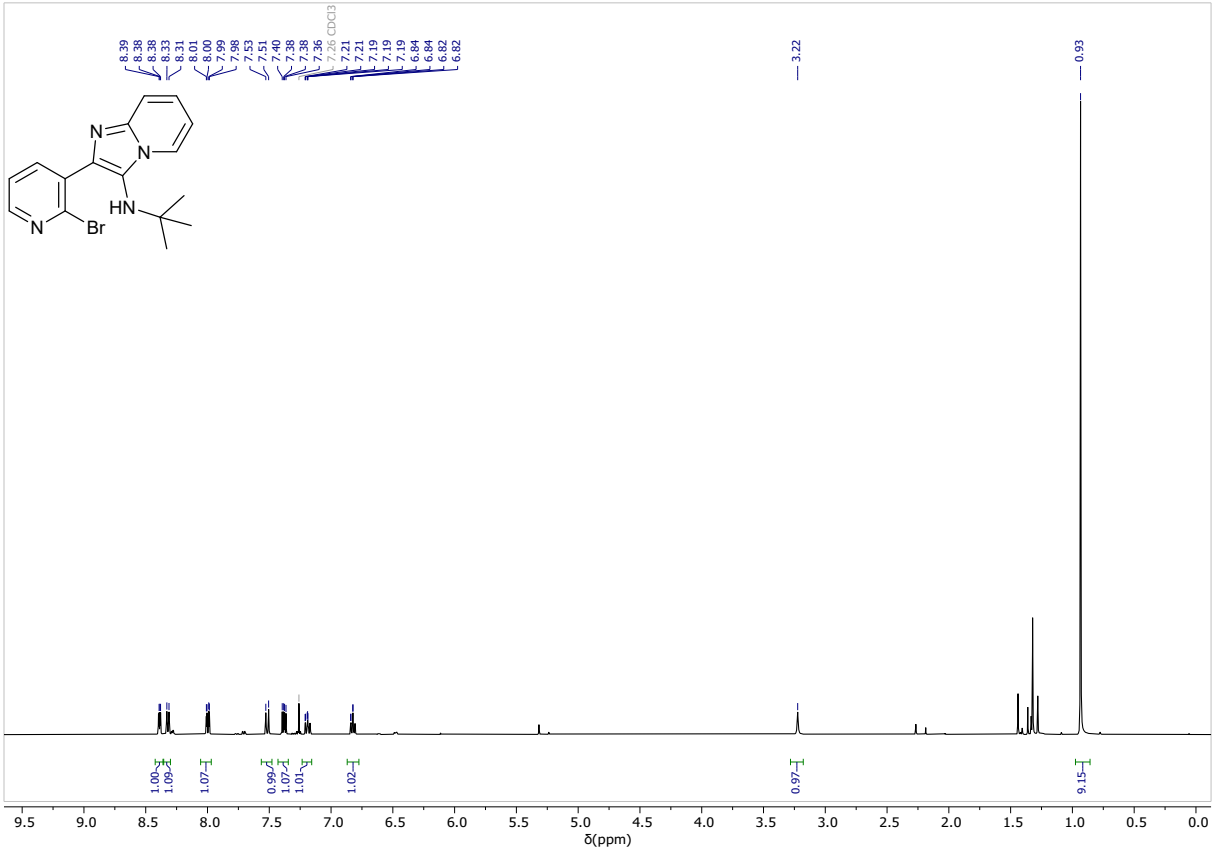


Figure 9 ***^{1}H-NMR-Spectrum of Compound 8.***

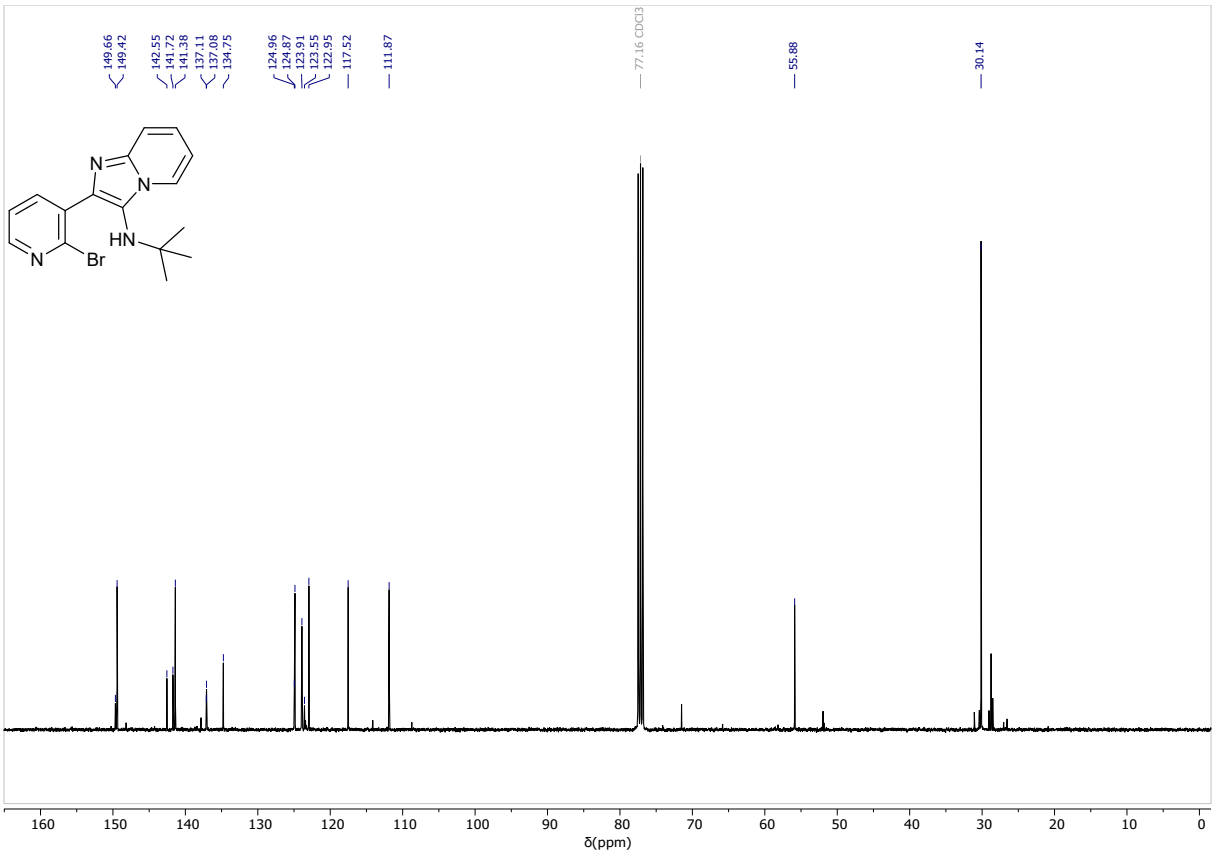


Figure 10 ***^{13}C-NMR-Spectrum of Compound 8.***

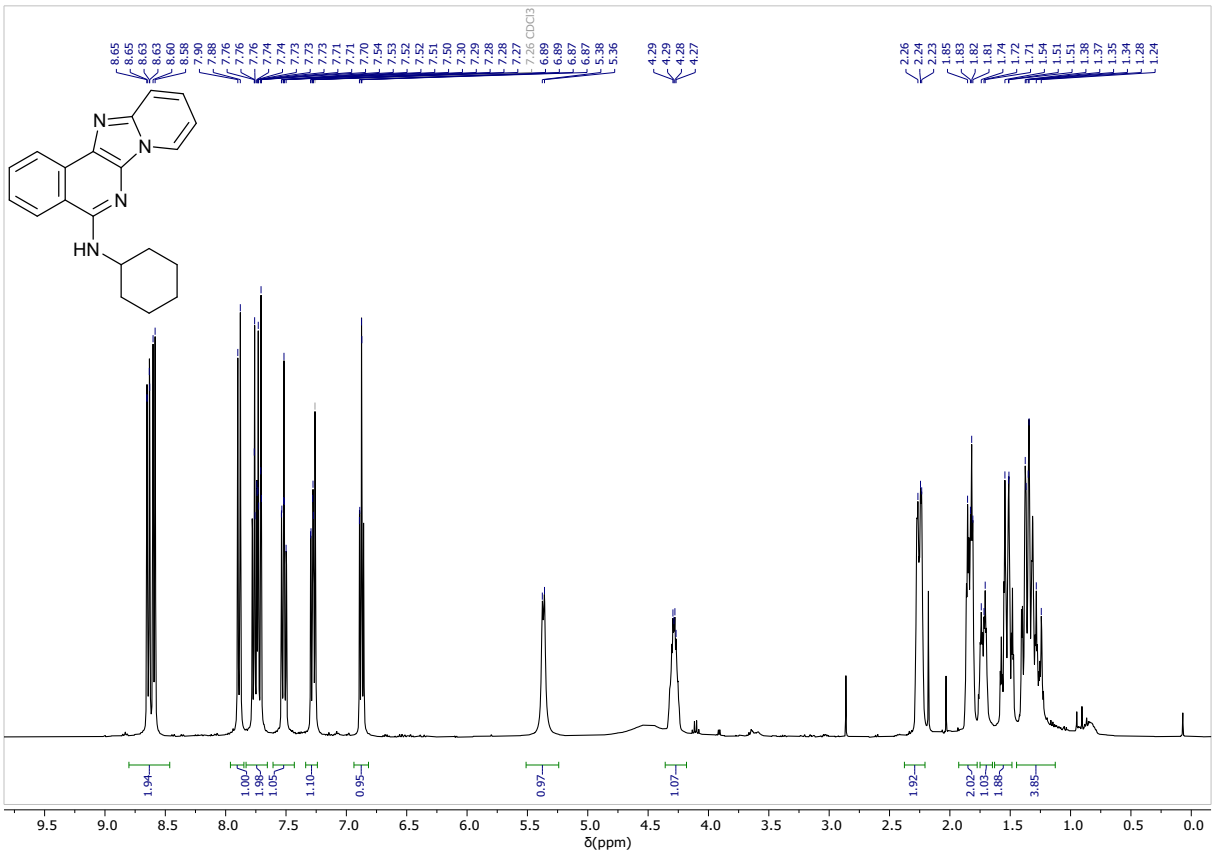


Figure 11 ***^{1}H-NMR-Spectrum of Compound 9a.***

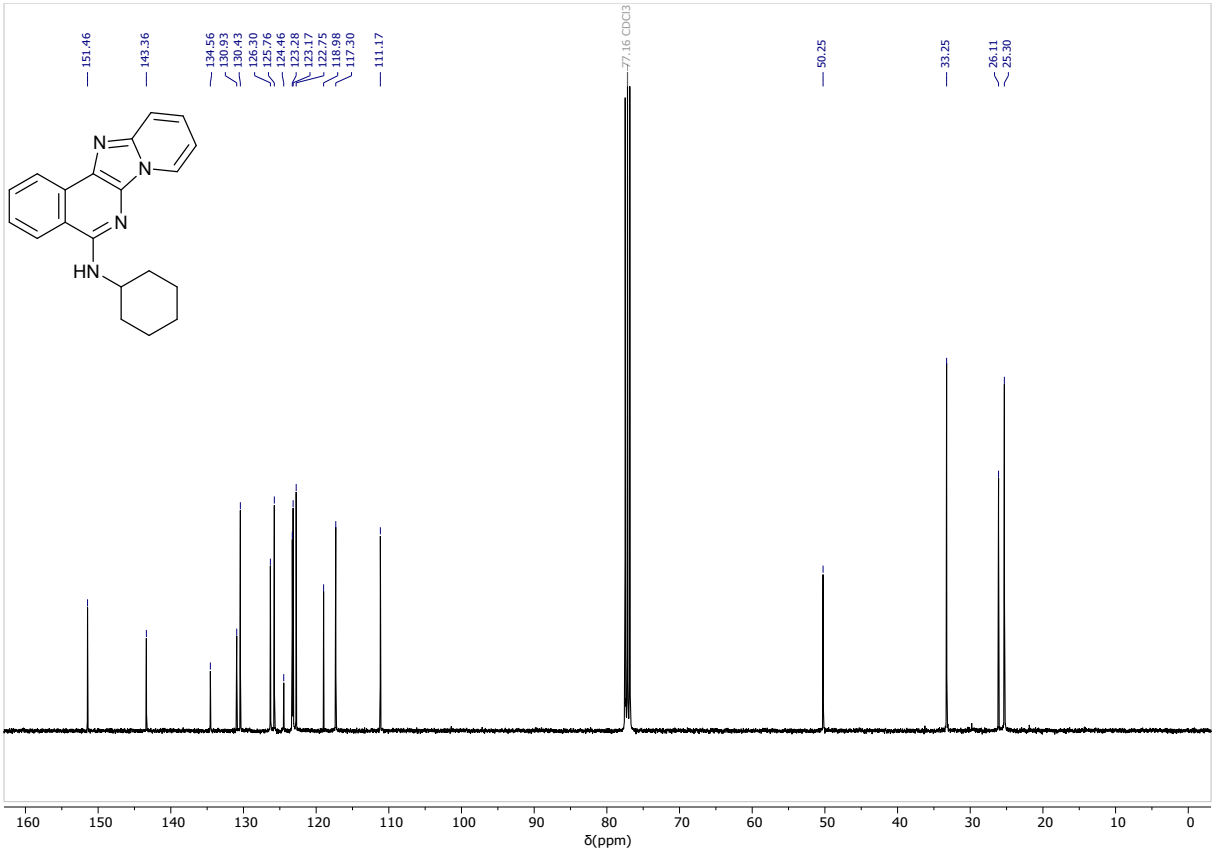


Figure 12 ***^{13}C-NMR-Spectrum of Compound 9a.***

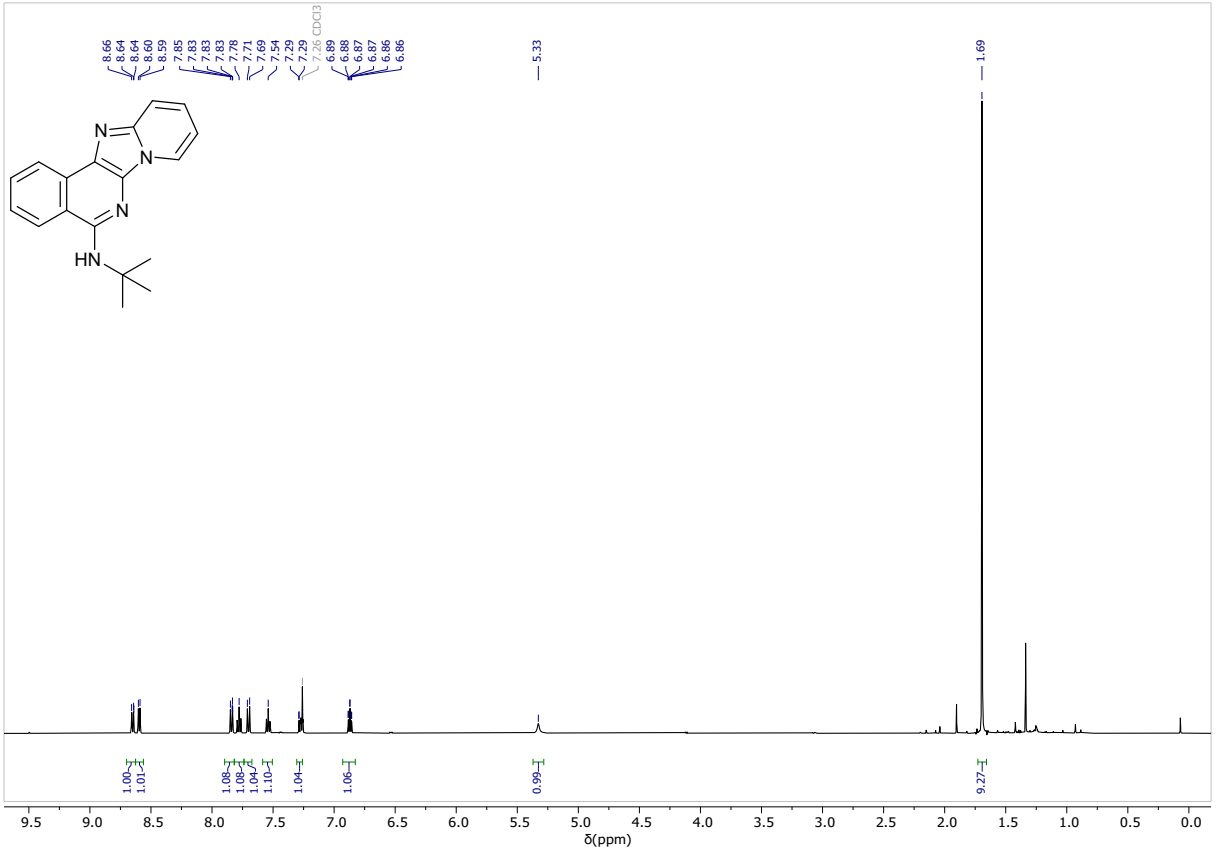


Figure 13 ***^{1}H-NMR-Spectrum of Compound 9b.***

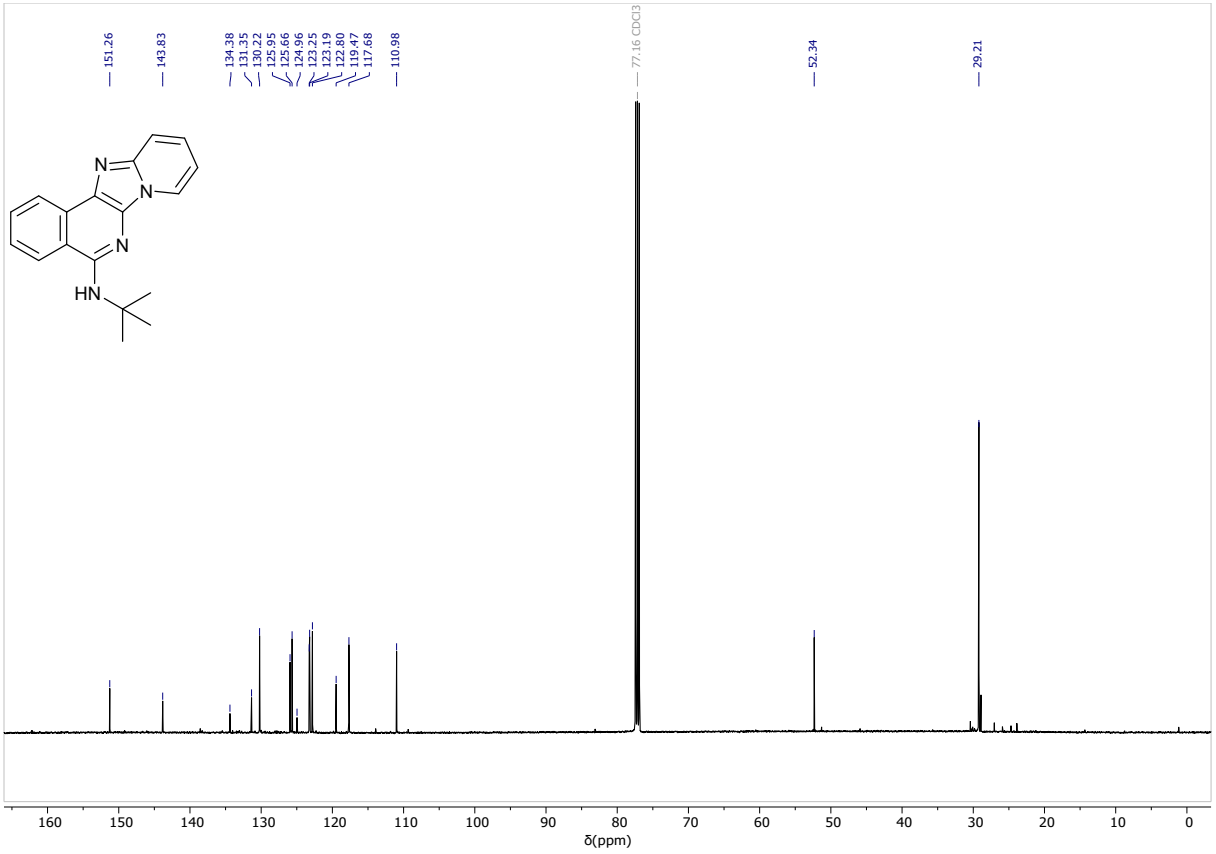


Figure 14 ***^{13}C-NMR-Spectrum of Compound 9b.***

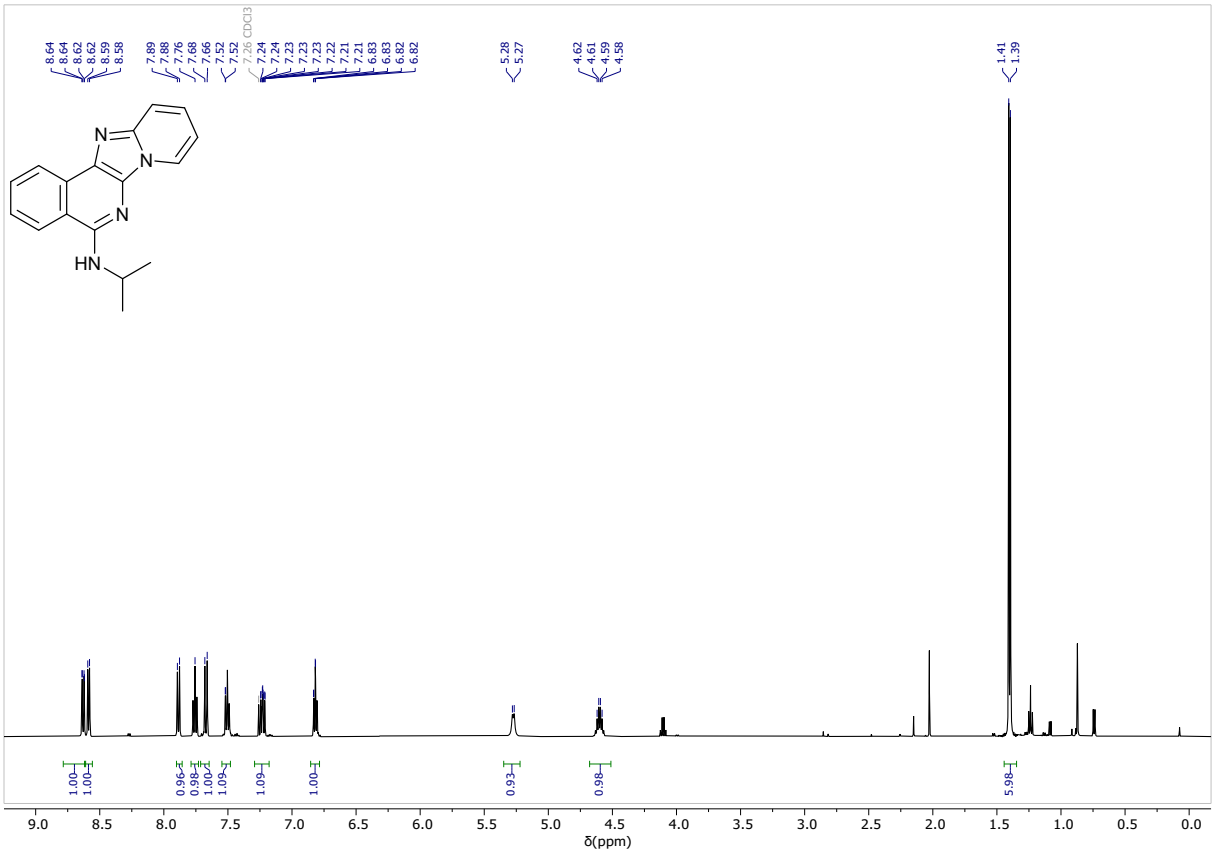


Figure 15 ***^{1}H-NMR-Spectrum of Compound 9c.***

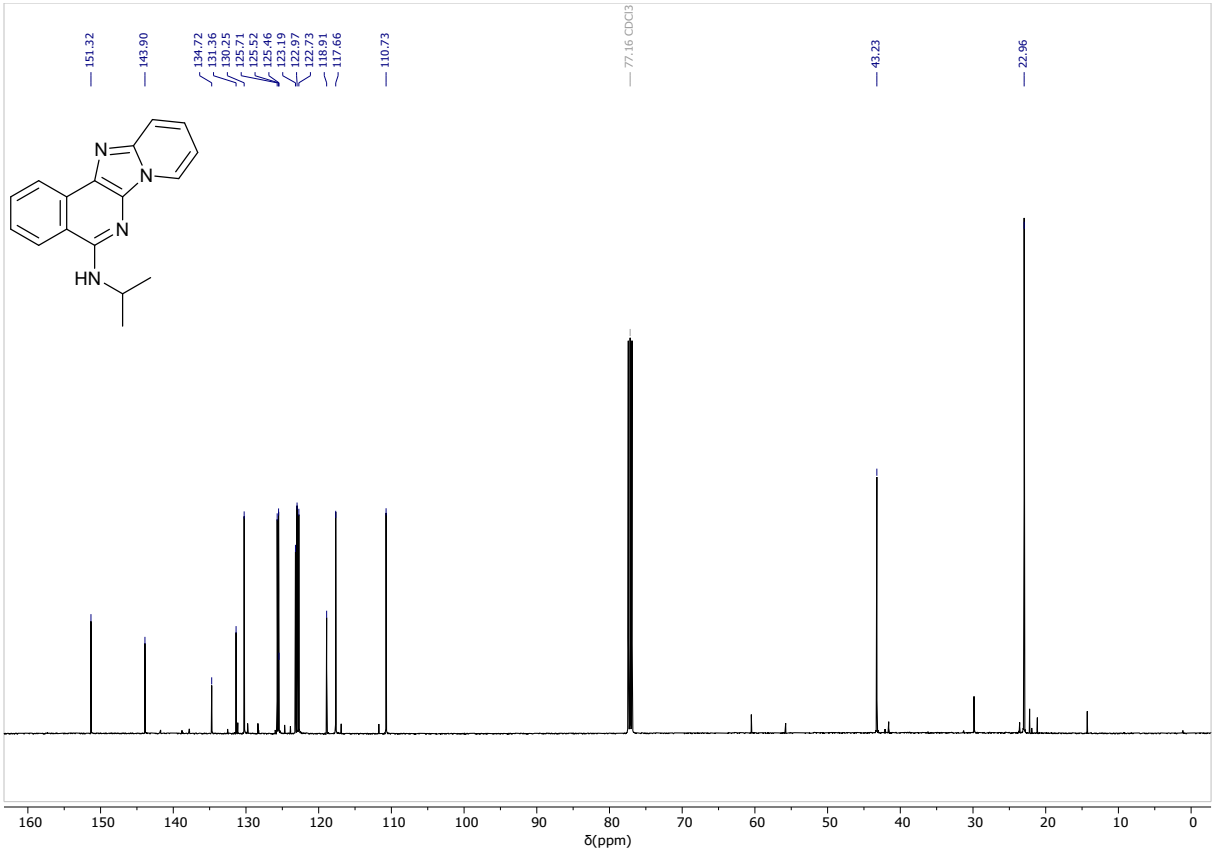


Figure 16 ***^{13}C-NMR-Spectrum of Compound 9c.***

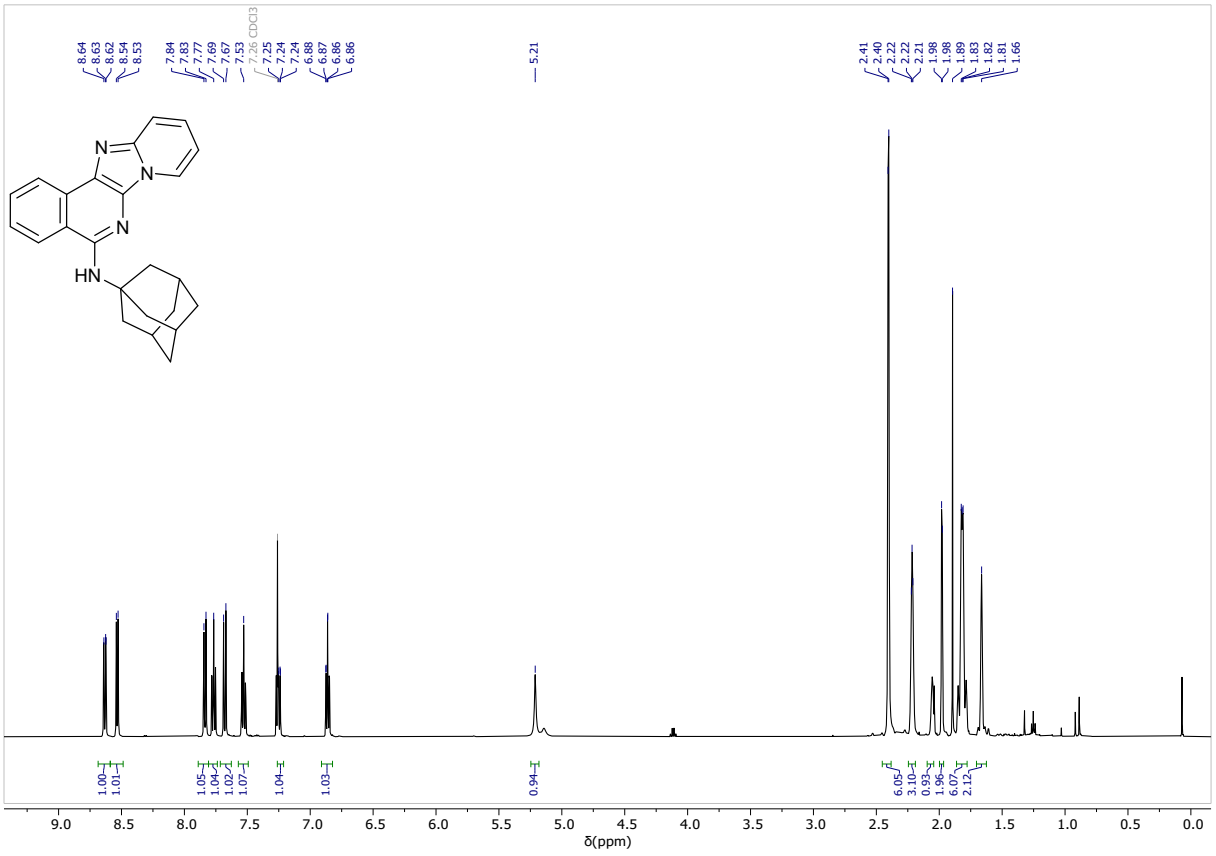


Figure 17 ***^{1}H-NMR-Spectrum of Compound 9d.***

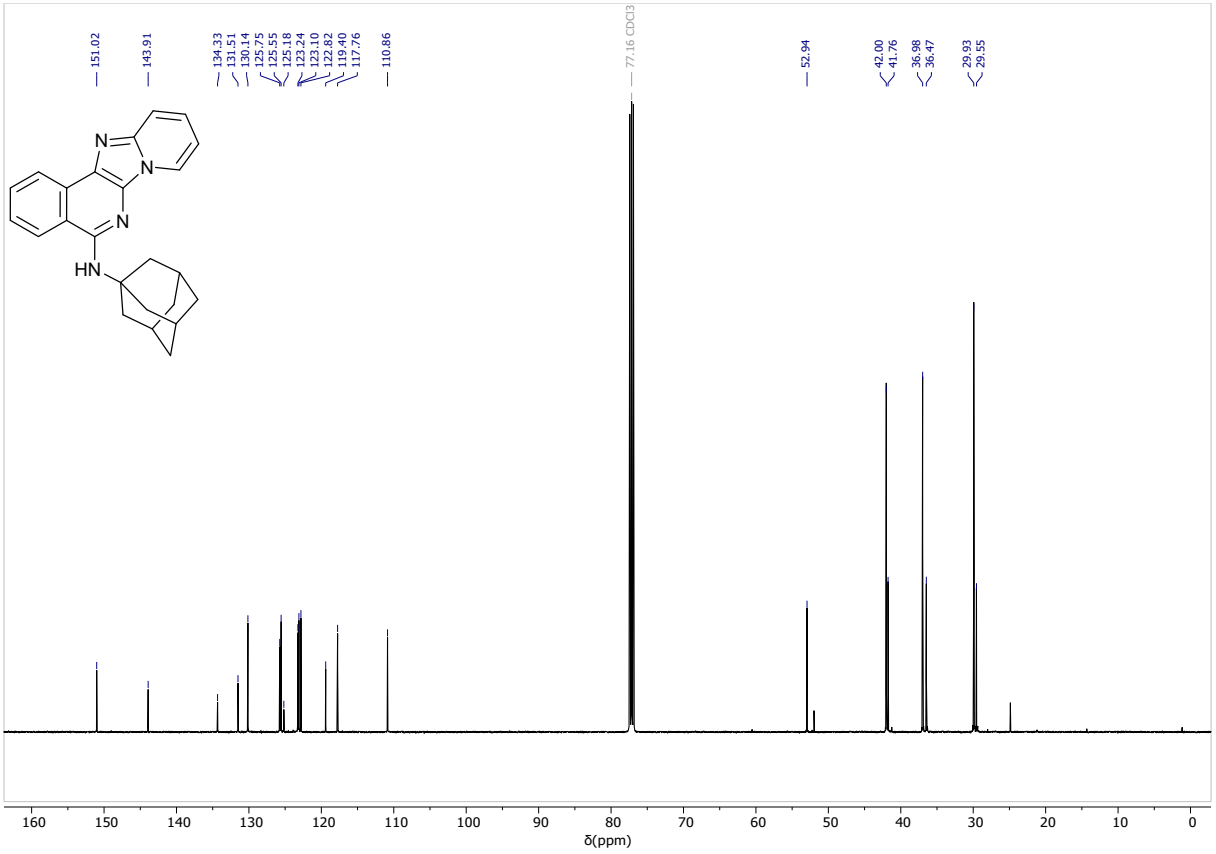


Figure 18 ***^{13}C-NMR-Spectrum of Compound 9d.***

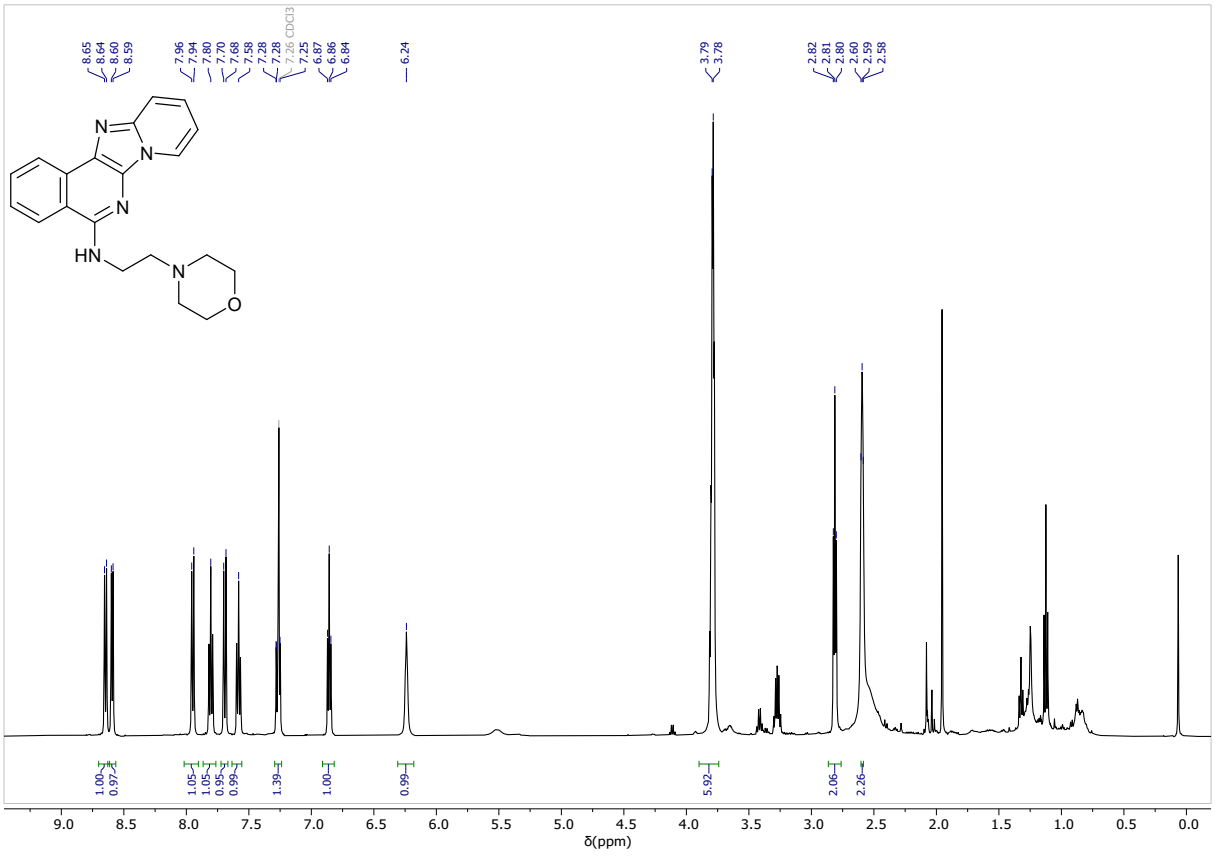


Figure 19 ***^{1}H-NMR-Spectrum of Compound 9e.***

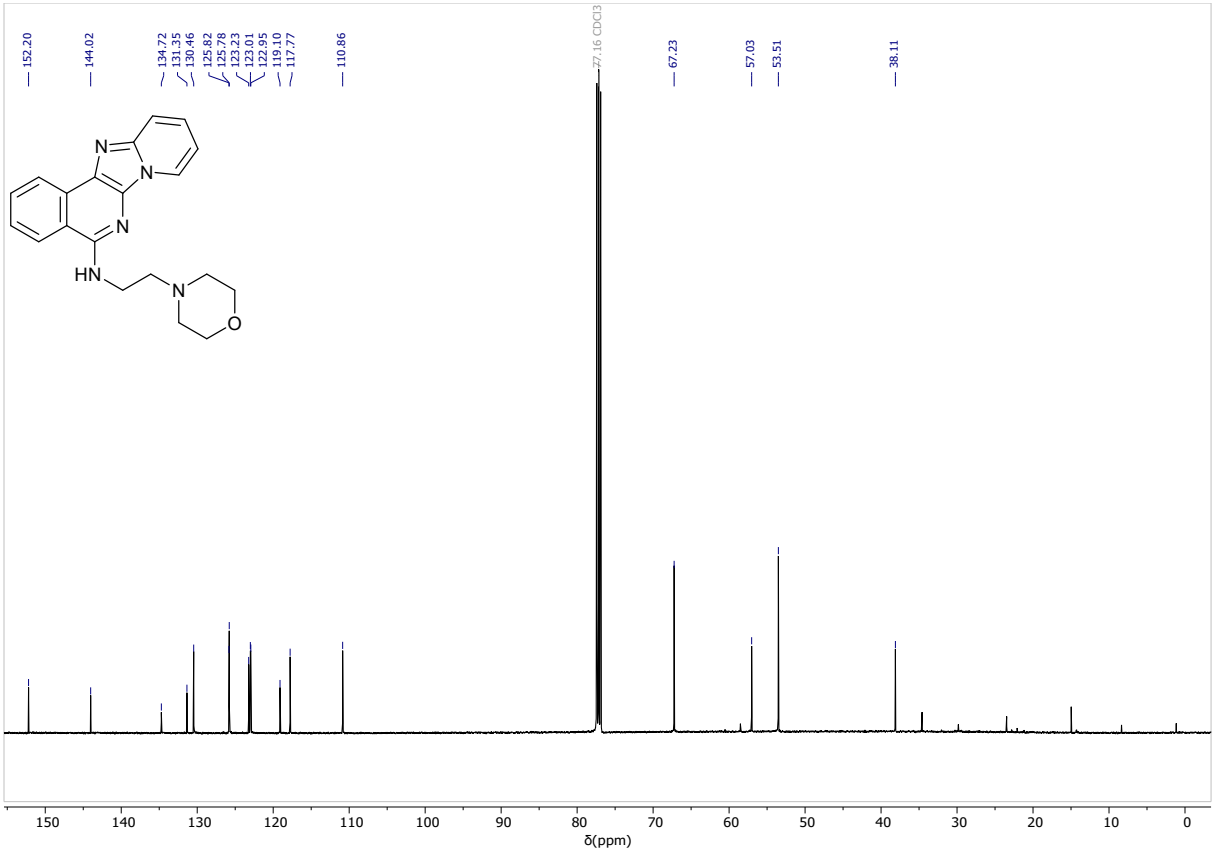


Figure 20 ***^{13}C-NMR-Spectrum of Compound 9e.***

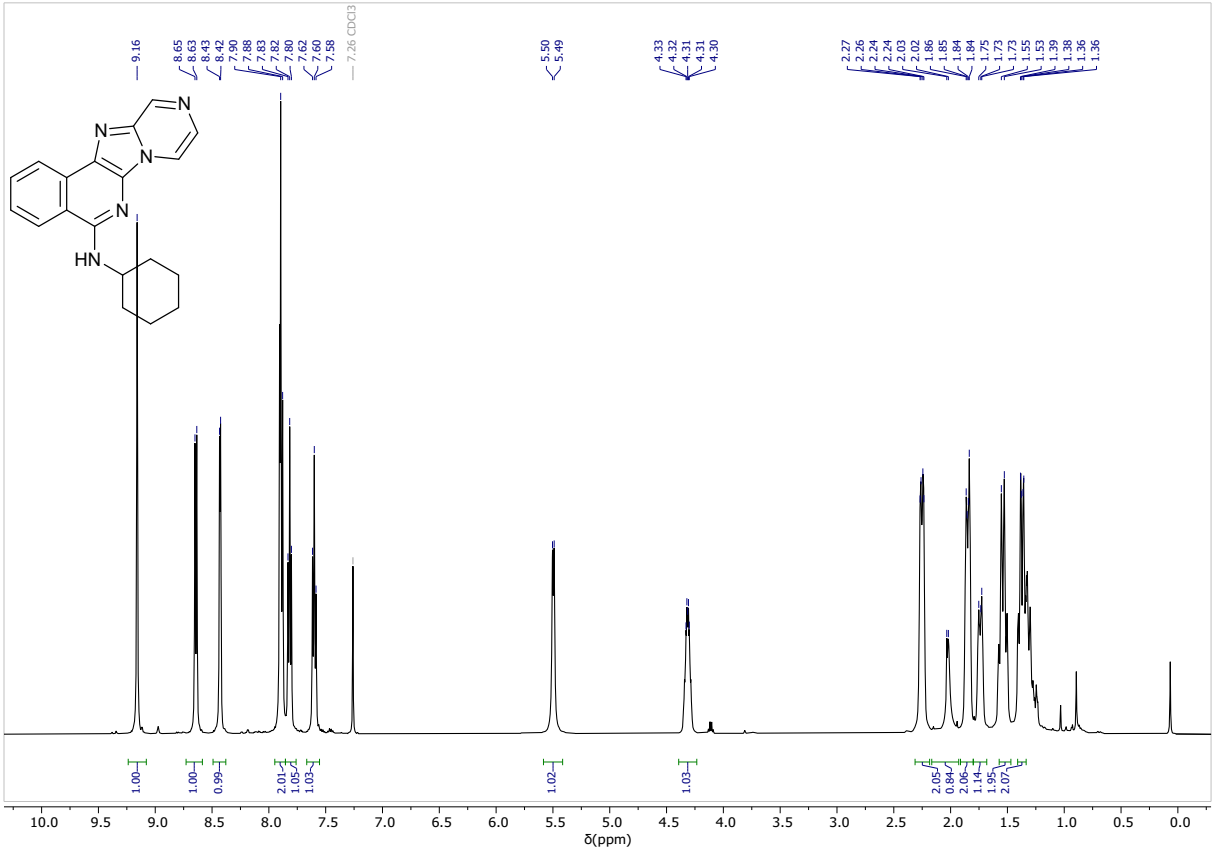


Figure 21 ***^{1}H-NMR-Spectrum of Compound 10a.***

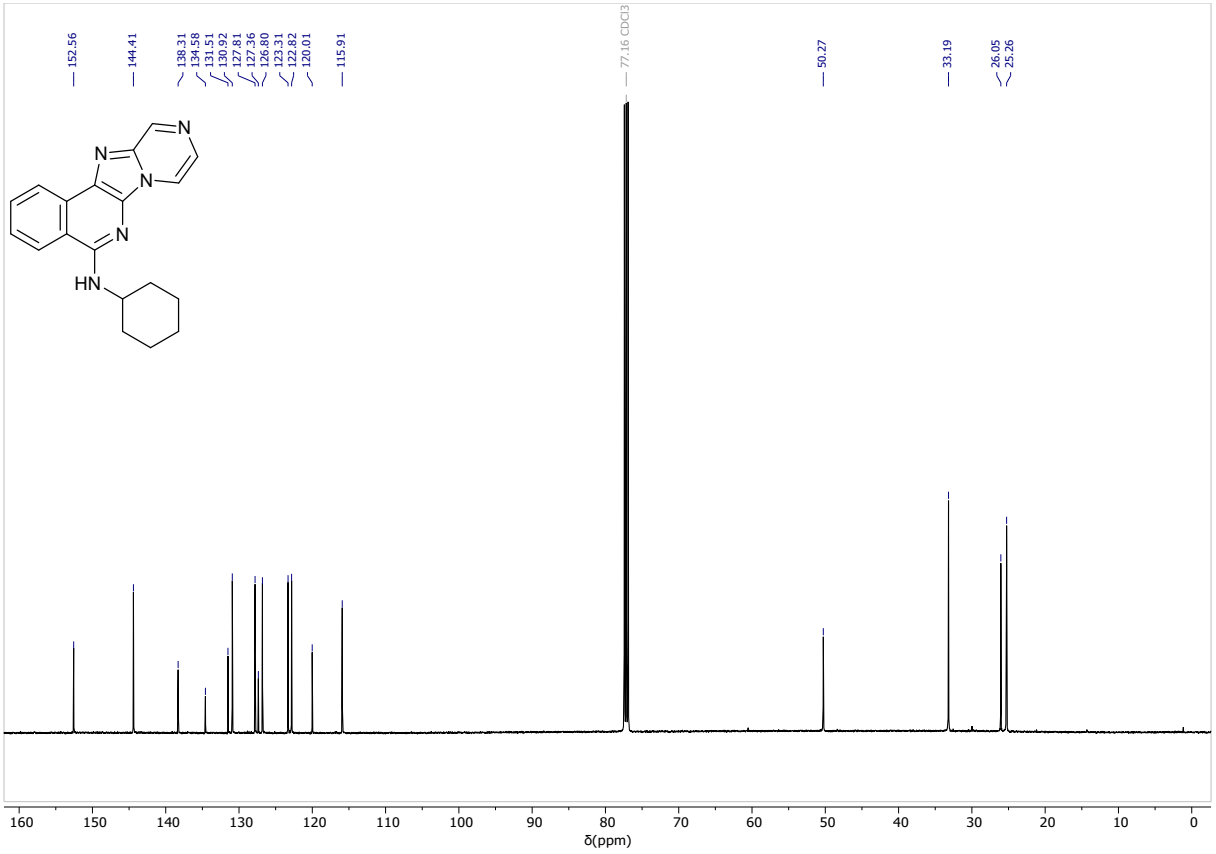


Figure 22 ***^{13}C-NMR-Spectrum of Compound 10a.***

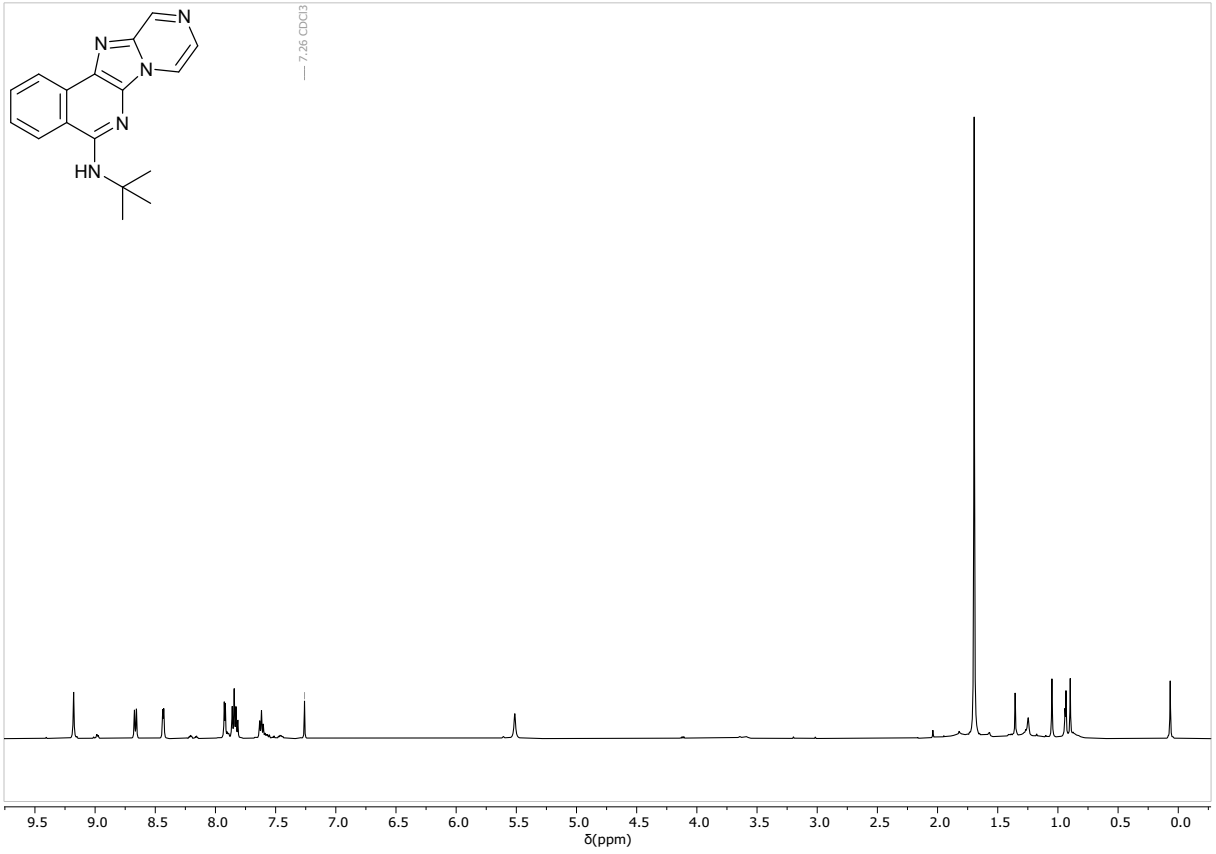
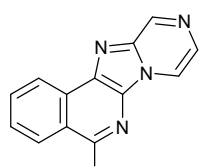


Figure 23 ***^{1}H-NMR-Spectrum of Compound 10b.***



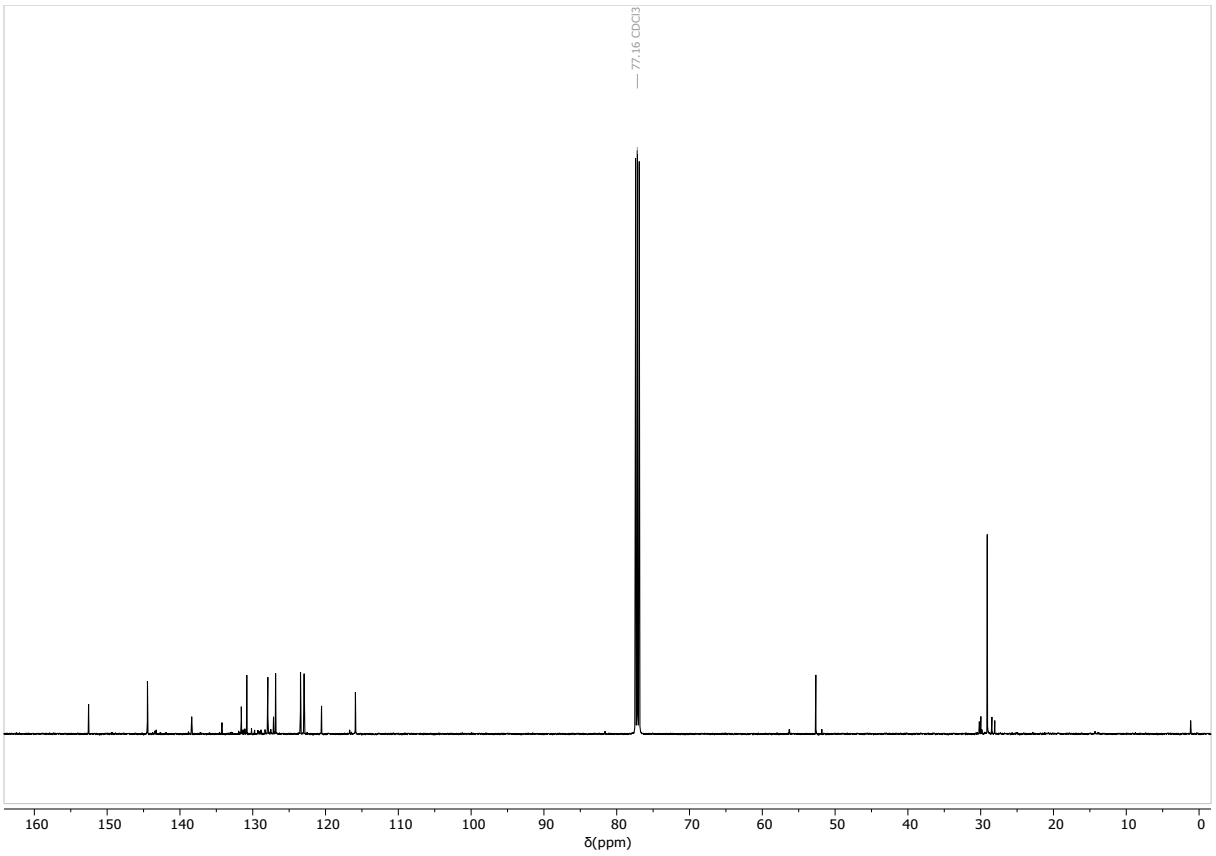


Figure 24 ***^{13}C-NMR-Spectrum of Compound 10b.***

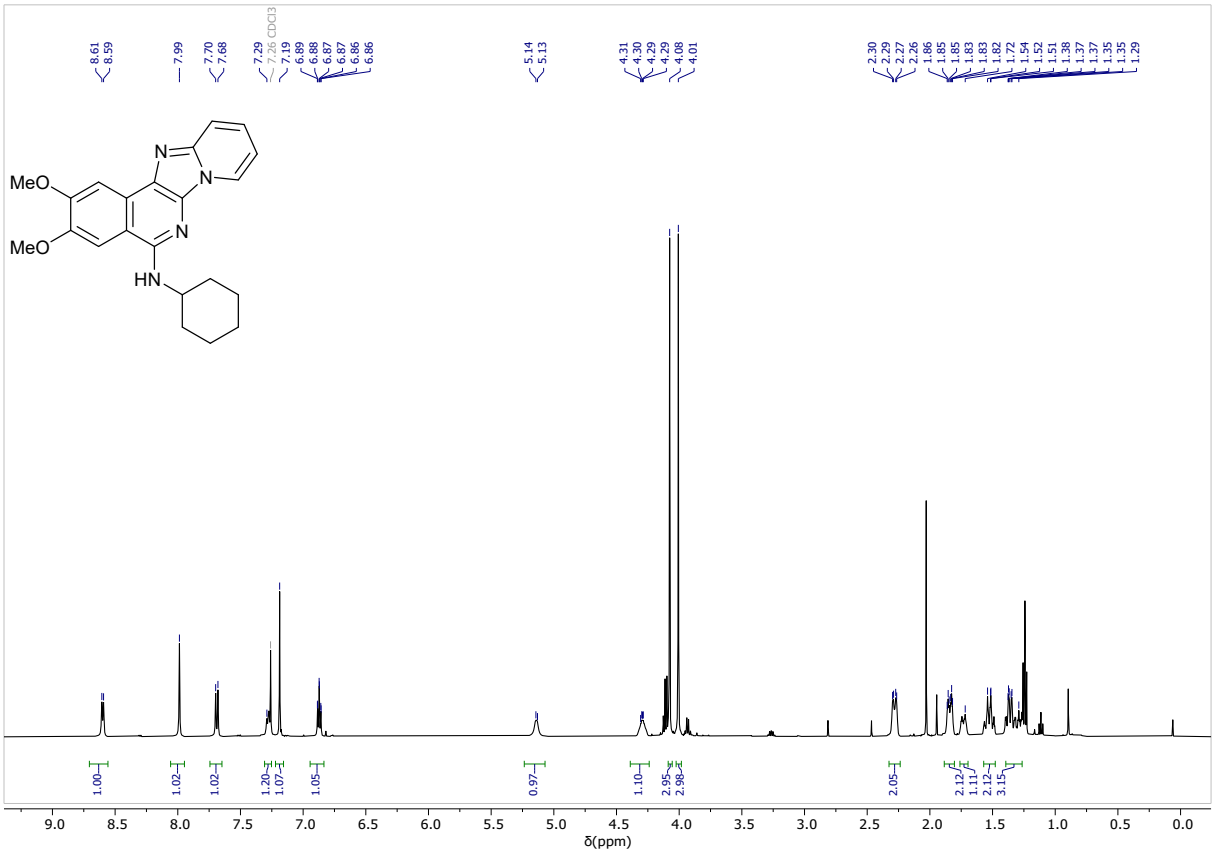


Figure 25 ***^{1}H-NMR-Spectrum of Compound 11a.***

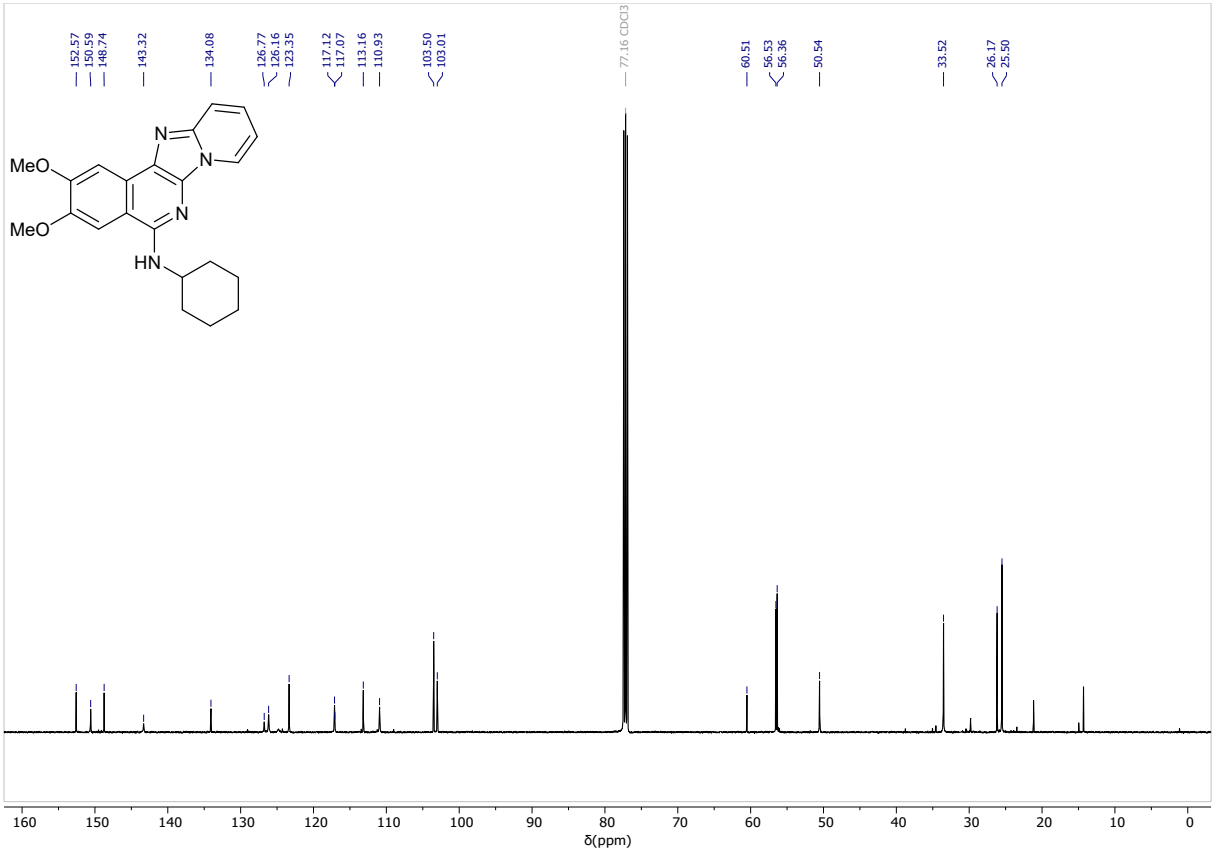


Figure 26 ***^{13}C-NMR-Spectrum of Compound 11a.***

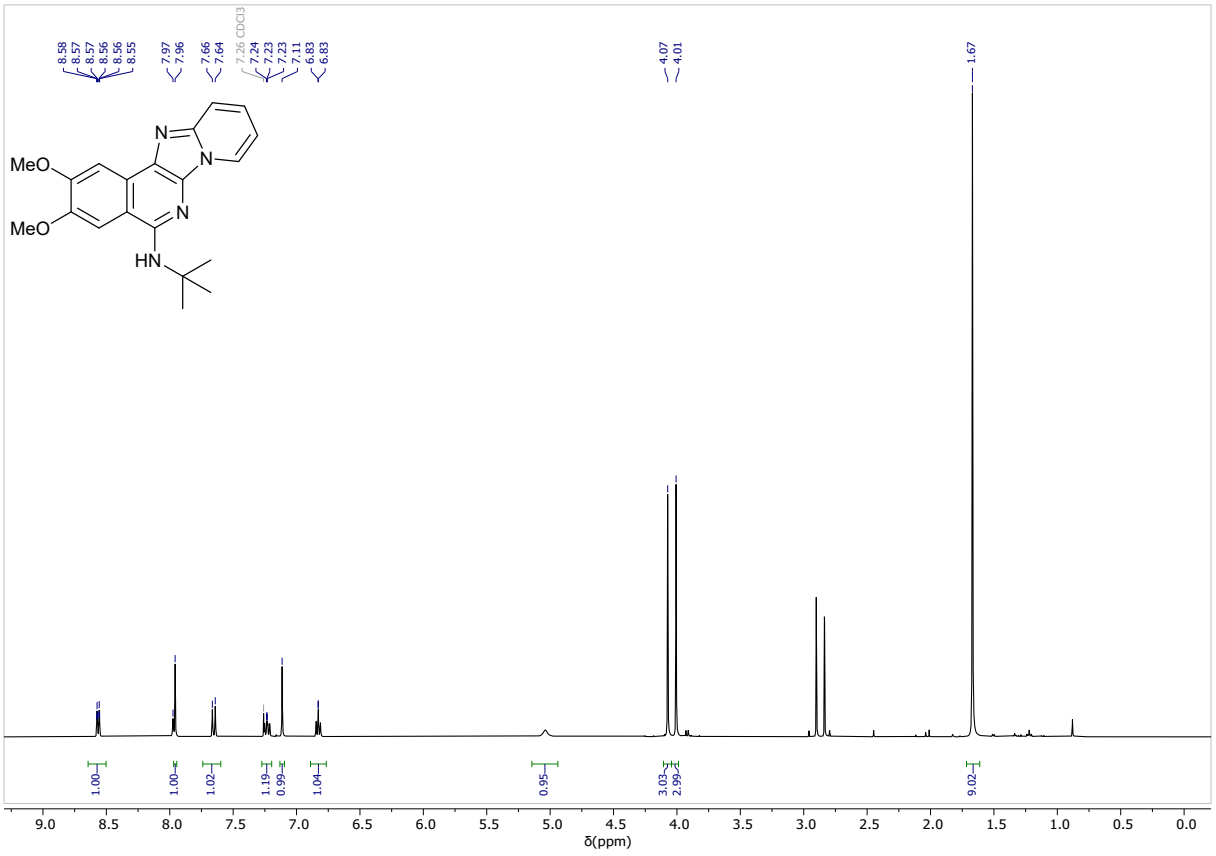


Figure 27 ***^{1}H-NMR-Spectrum of Compound 11b.***

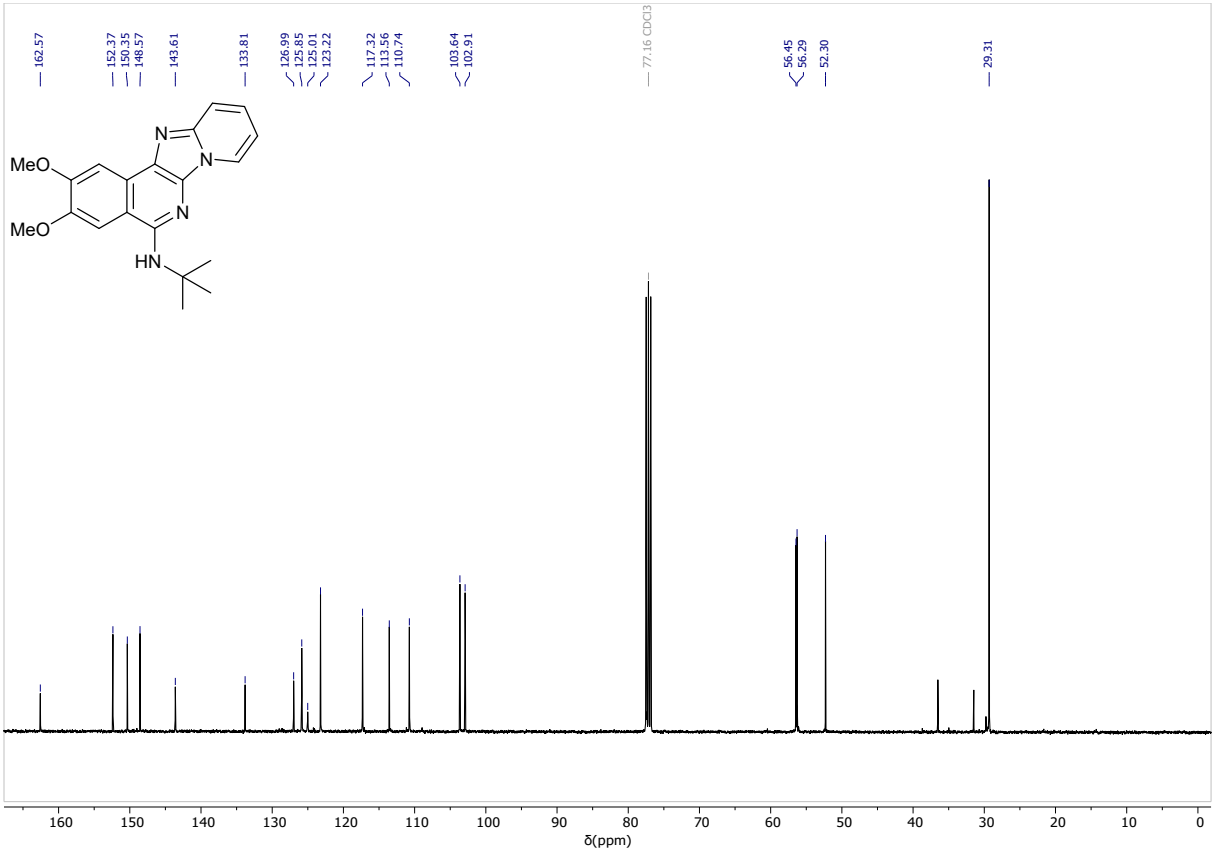


Figure 28 ***^{13}C-NMR-Spectrum of Compound 11b.***

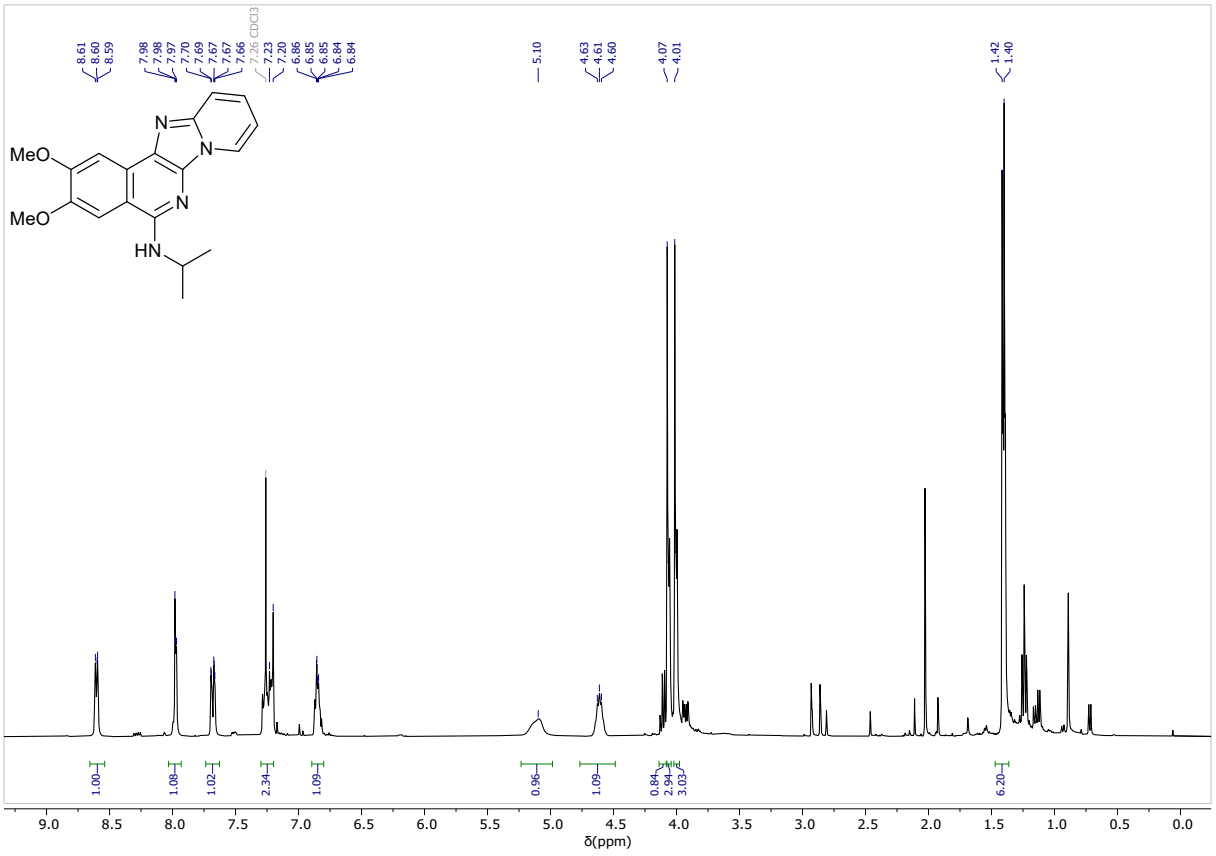


Figure 29 ***^{1}H-NMR-Spectrum of Compound 11c.***

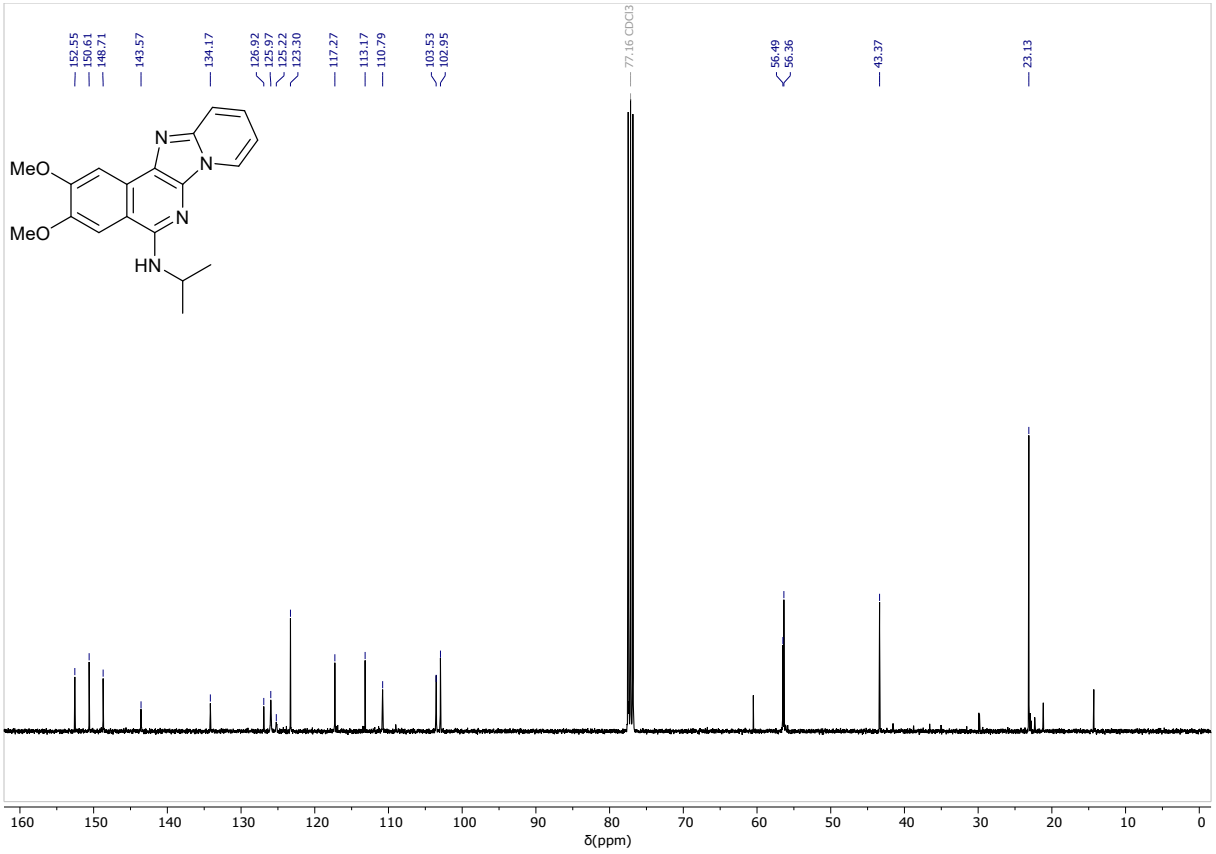


Figure 30 ***^{13}C-NMR-Spectrum of Compound 11c.***

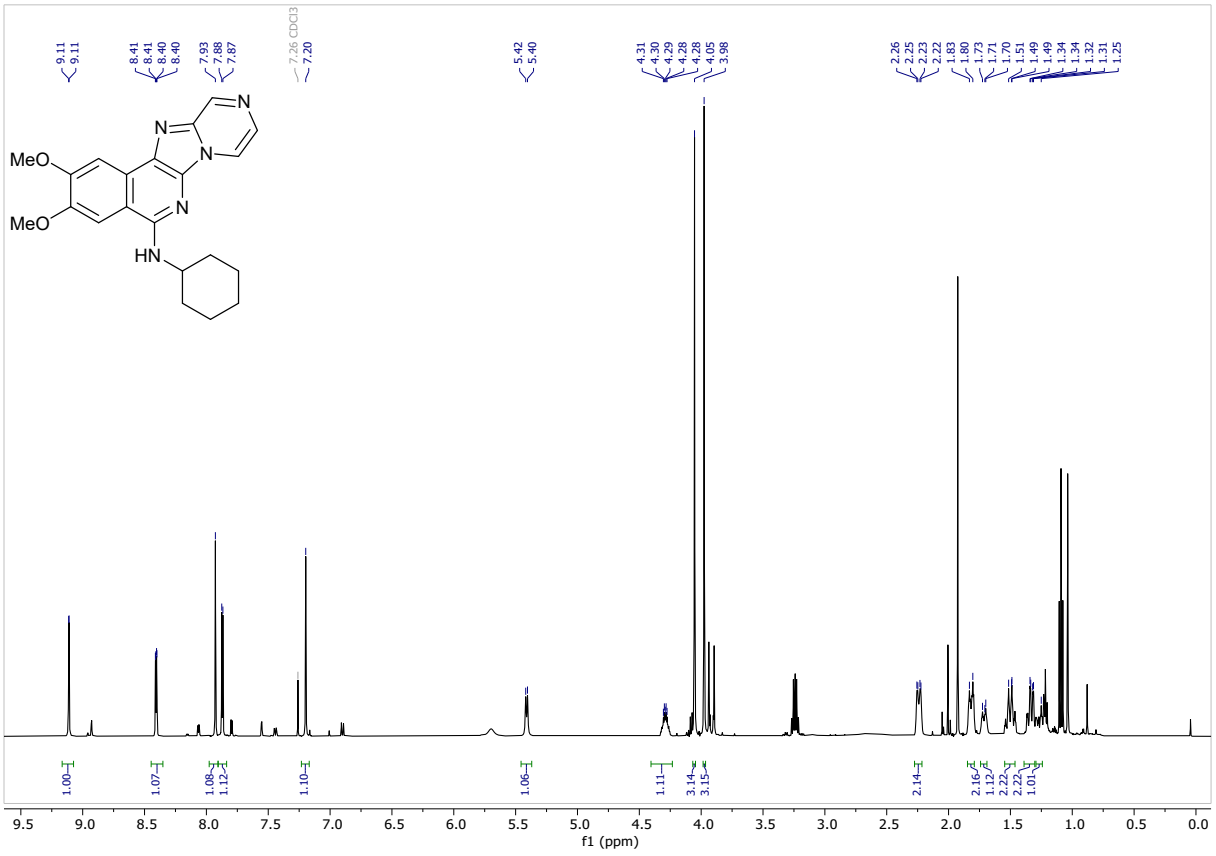


Figure 31 Ins 4a ***^{1}H-NMR-Spectrum of Compound 12a.***

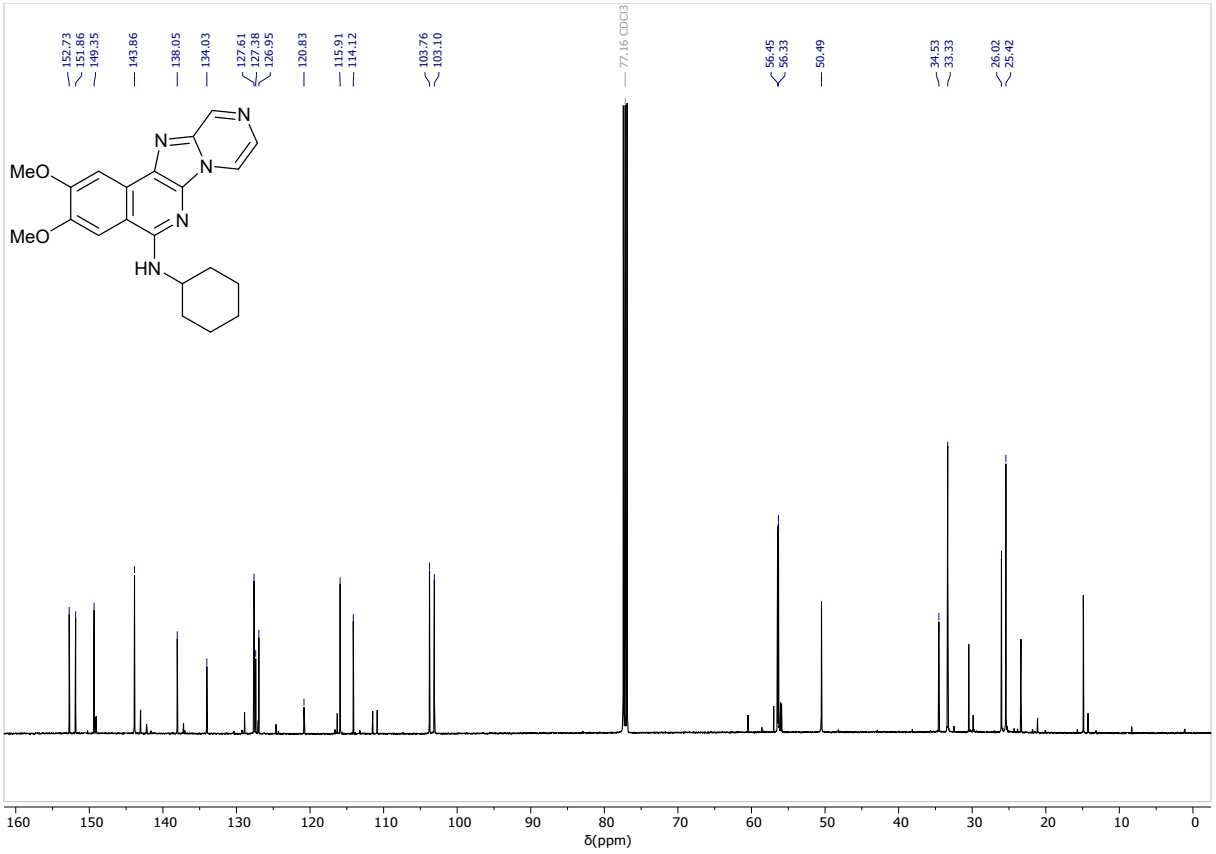


Figure 32 ***^{13}C-NMR-Spectrum of Compound 12a.***

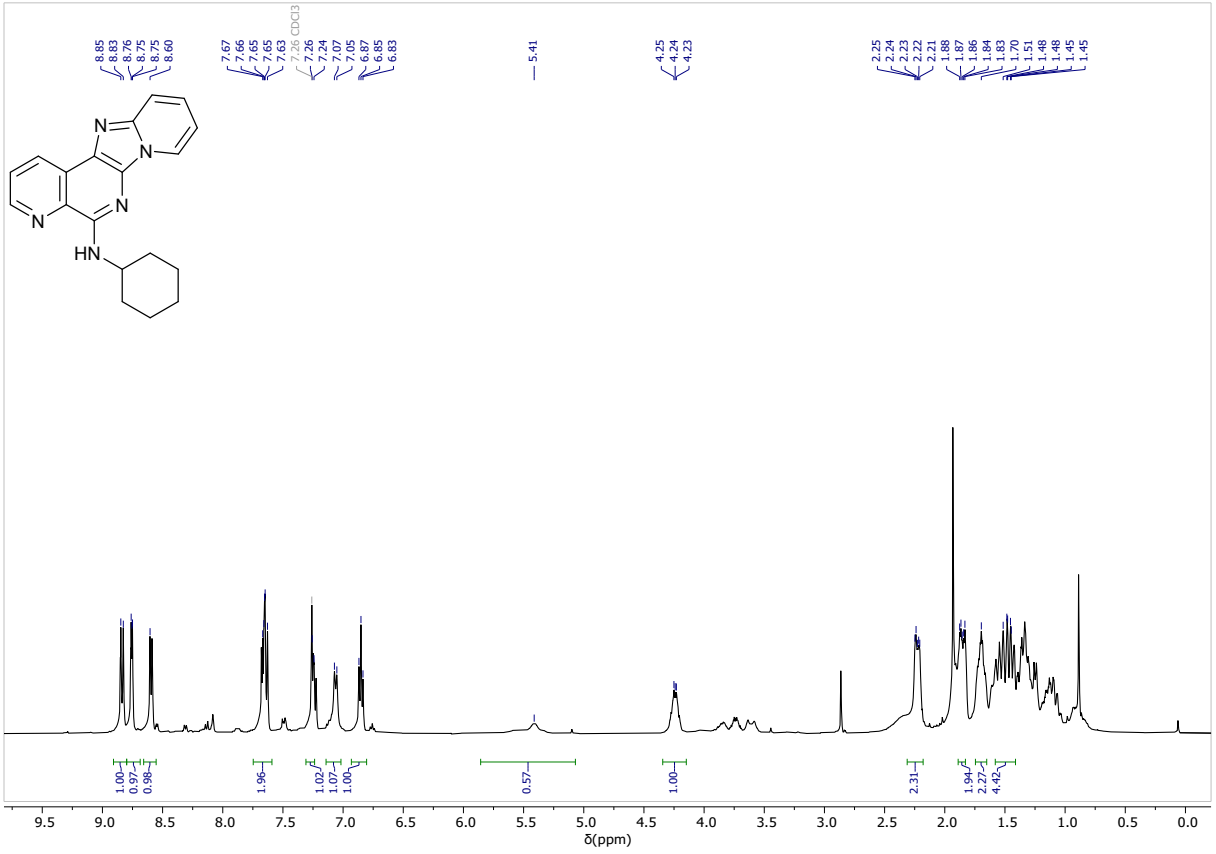


Figure 33 ***^{1}H-NMR-Spectrum of Compound 13a.***

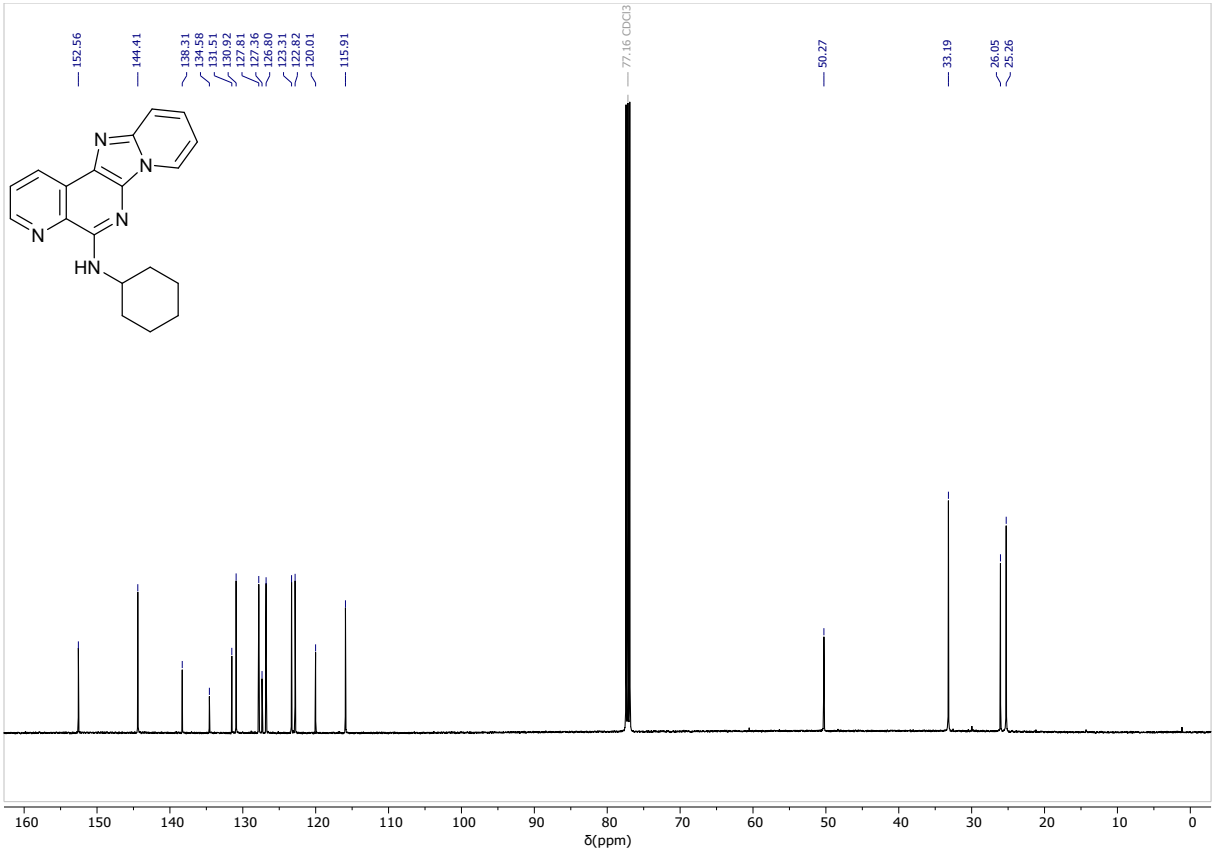


Figure 34 ***^{13}C-NMR-Spectrum of Compound 13a.***

Crystal Structure Determination of compound 9d and 10a

The single-crystal X-ray diffraction study was carried out on a Bruker D8 Venture diffractometer with a PhotonII detector at 173(2) K or 298(2) K using Cu-K radiation (= 1.54178 Å). Dual space methods (SHELXT) [G. M. Sheldrick, *Acta Crystallogr.* 2015, **A71**, 3-8] were used for structure solution, and refinement was carried out using SHELXL-2014 (full-matrix least-squares on F^2) [G. M. Sheldrick, *Acta Crystallogr.* 2015, **C71**, 3-8]. Hydrogen atoms were localized by difference electron density determination and refined using a riding model (H(N) free). Semi-empirical absorption corrections were applied.

9d: yellow crystals, $C_{24}H_{24}N_4$, M_r = 368.47, crystal size 0.24 × 0.12 × 0.03 mm, monoclinic, space group $P2_1/n$ (No. 14), a = 6.5540(6) Å, b = 12.6859(12) Å, c = 23.2169(21) Å, β = 97.357(4)°, V = 1914.4(3) Å^3, Z = 4, ρ = 1.278 Mg/m^{-3}, μ(Cu-K$_\alpha$) = 0.60 mm^{-1}, F(000) = 784, T = 298 K, $2\theta_{max}$ = 144.2°, 26584 reflections, of which 3764 were independent (R_{int} = 0.029), 256 parameters, R_1 = 0.039 (for 3445 I > 2σ(I)), wR_2 = 0.097 (all data), S = 1.03, largest diff. peak / hole = 0.18 / -0.18 e Å^{-3}.

10a: yellow crystals, $C_{19}H_{19}N_5$, M_r = 317.39, crystal size 0.30 × 0.18 × 0.12 mm, monoclinic, space group $P2_1/c$ (No. 14), a = 7.7193(2) Å, b = 19.0741(6) Å, c = 10.7854(3) Å, β = 103.055(1)°, V = 1546.98(8) Å^3, Z = 4, ρ = 1.363 Mg/m^{-3}, μ(Cu-K$_\alpha$) = 0.67 mm^{-1}, F(000) = 672, T = 123 K, $2\theta_{max}$ = 144.6°, 27211 reflections, of which 3049 were independent (R_{int} = 0.026), 220 parameters, 1 restraint, R_1 = 0.034 (for 2978 I > 2σ(I)), wR_2 = 0.085 (all data), S = 1.03, largest diff. peak / hole = 0.27 / -0.21 e Å^{-3}.

CCDC 2152372 (**9d**), and 2152373 (**10a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

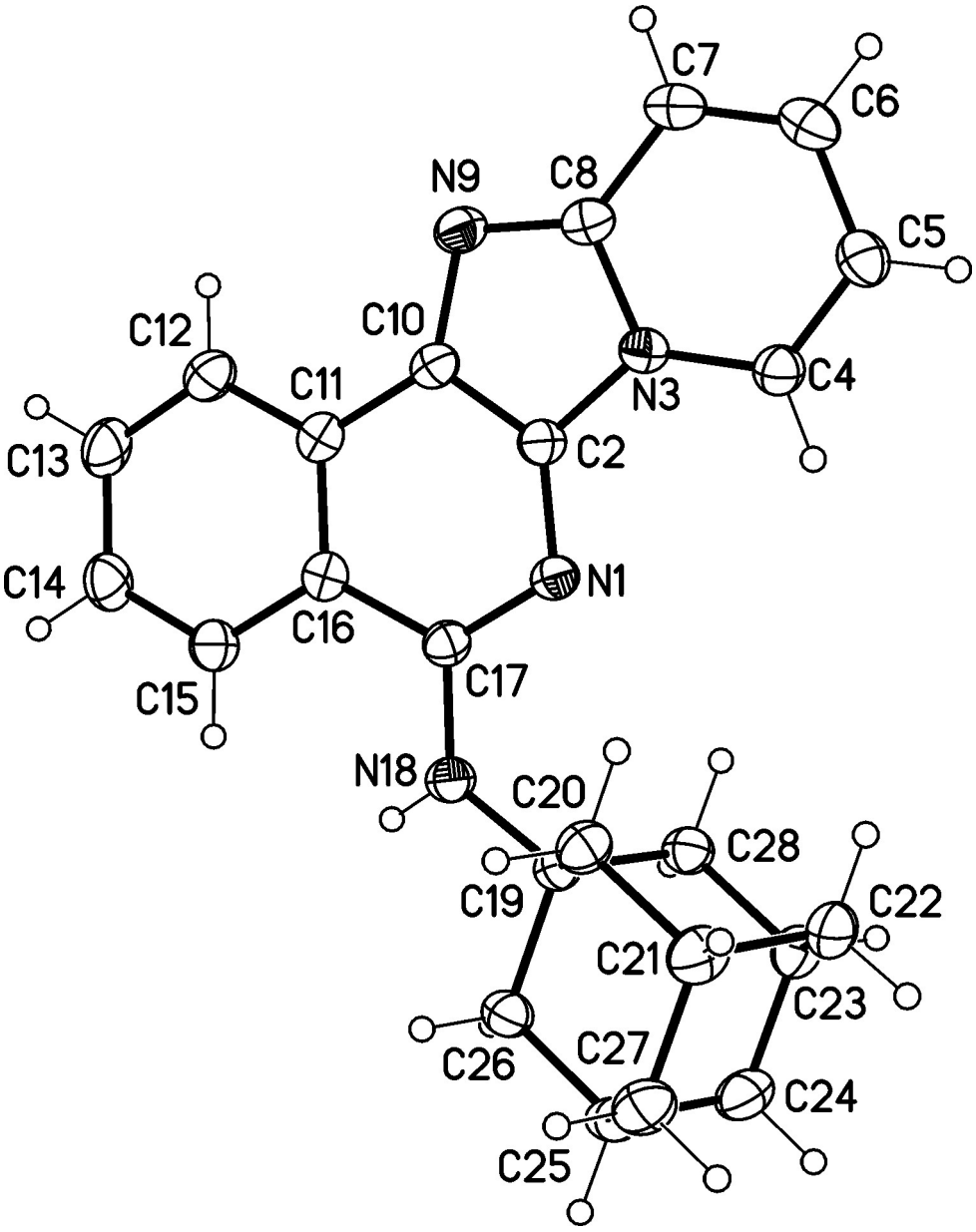


Fig. 1x. Molecular structure of **9d** (displacement parameters are drawn at 30 % probability level).

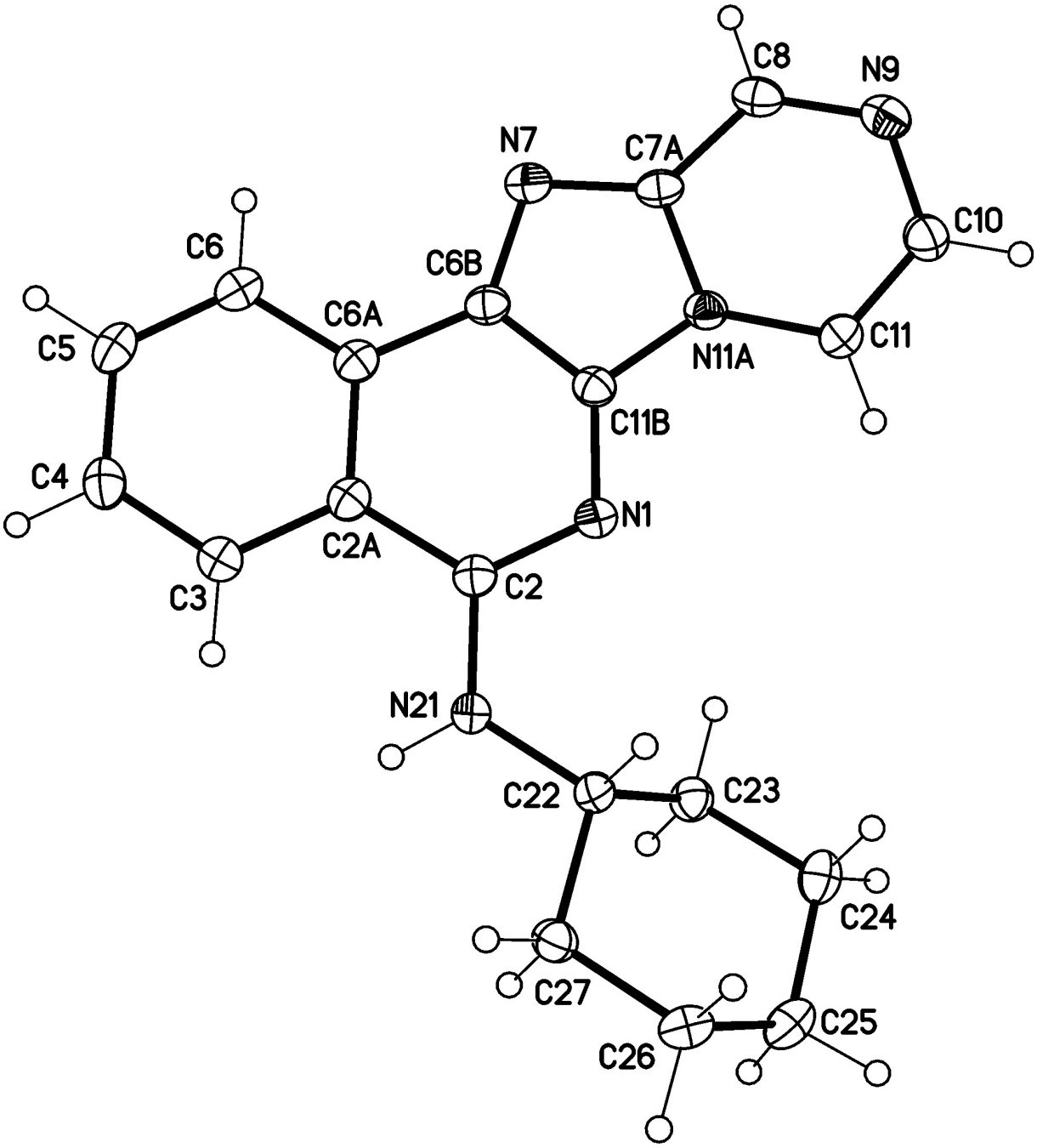


Fig. 2x. Molecular structure of **10a** (displacement parameters are drawn at 50 % probability level).